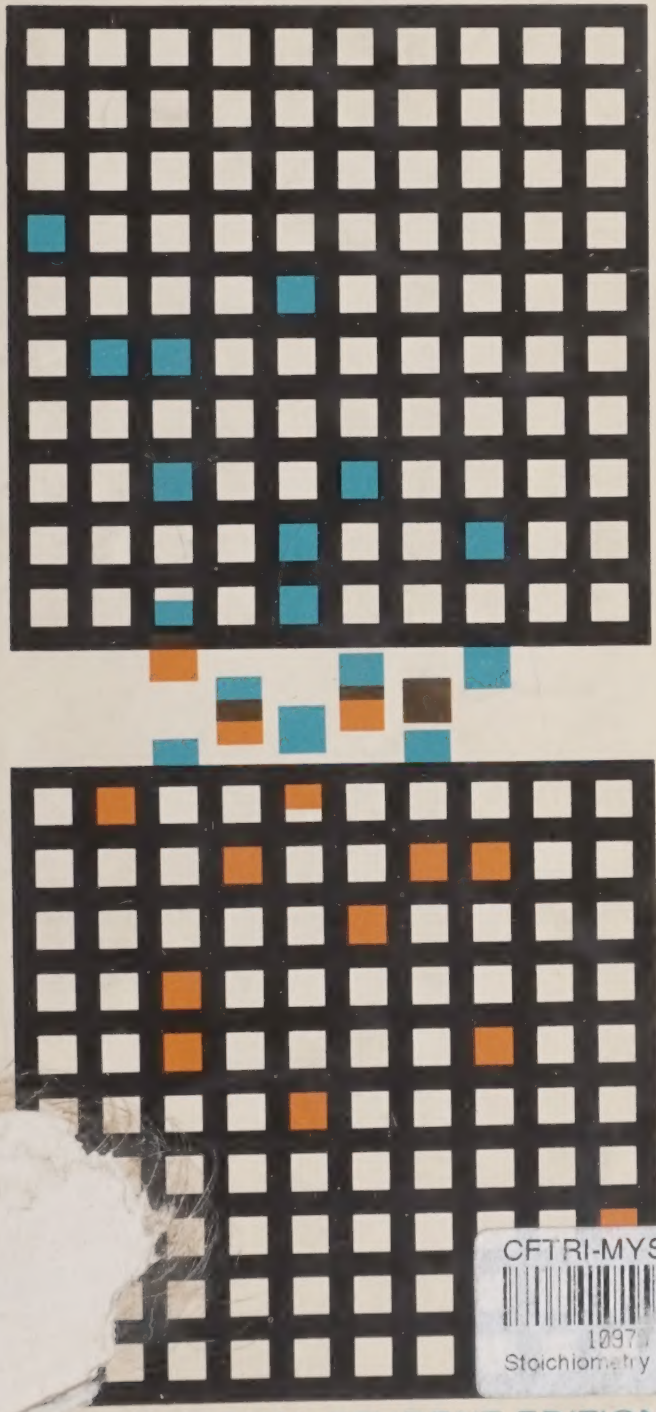
STOICHIOMETRY

FOR CHEMICAL ENGINEERS

EDWIN WILLIAMS & CURTIS JOHNSON



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STOICHIOMETRY
FOR CHEMICAL ENGINEERS

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After several meetings, this first Editorial Advisory Board submitted its report to the McGraw-Hill Book Company in September, 1925. In it were detailed specifications for a correlated series of more than a dozen texts and reference books which have since become the McGraw-Hill Series in Chemical Engineering.

Since its origin the Editorial Advisory Board has been benefited by the guidance and continuing interest of such other distinguished chemical engineers as Manson Benedict, John R. Callaham, Arthur W. Hixson, H. Fraser Johnstone, Webster N. Jones, Paul D. V. Manning, Albert E. Marshall, Charles M. A. Stine, Edward R. Weidlein, and Walter G. Whitman. No small measure of credit is due not only to the pioneering members of the original board but also to those engineering educators and industrialists who have succeeded them in the task of building a permanent literature for the chemical engineering profession.

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STOICHIOMETRY

for Chemical Engineers

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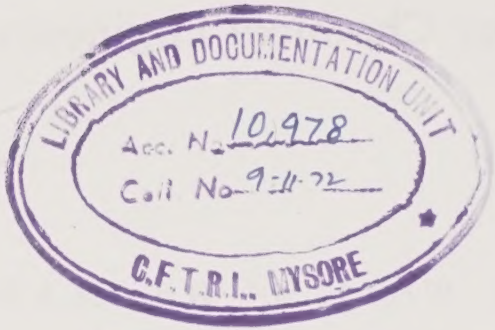

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Stoichiometry fo

TOSHO PRINTING CO., LTD.
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To our wives, *Julie and Kay,*
for pacing the floor while we labored

PREFACE

The word *stoichiometry* is derived from the Greek words "stoicheion" meaning an element and "metron" meaning measure. Stoichiometry is that branch of chemistry which deals with the combining proportions of the elements or compounds involved in chemical reactions. The basic principle of stoichiometry is the law of definite and multiple proportions. It states that a pure chemical substance always contains its elements in the same proportions by weight and that, when two elements unite to form a series of compounds, the weights of one element combining with a fixed weight of the other are simple integral multiples of each other.

The law was vaguely expounded by Jeremias Benjamin Richter in his book "Anfangsgründe der Stoichiometrie" in 1793. He had made a study of neutralization reactions and had compiled tables showing the quantities of different bases which would neutralize 1,000 parts of a given acid, and vice versa, and had shown that the numbers involved were proportional. Professor F. J. Moore* wrote: "In his book Richter confused these valuable ideas with fanciful speculations of no importance; his language was archaic, and his style such as might have been expected from a man who would invent the word stoichiometry."

Although the term "stoichiometry" originally meant only the application of the law of definite and multiple proportions, its meaning has been broadened by common usage.

A pioneer textbook† in the field contains this statement in the introduction: "Industrial stoichiometry is the application of the laws of the conservation of matter, of the elements and of energy, and of the chemical laws of combining weights to the processes and operations of industrial chemistry." Note that the definition now permits the inclusion of an operation, such as crystallization, in which no chemical reaction occurs and in which stoichiometry, in its original sense, plays no part. Furthermore, the processes and operations of industrial chemistry usually cannot be handled solely by the laws of conservation of mass and energy and

* "A History of Chemistry," 3d ed., p. 109, McGraw-Hill Book Company, Inc., New York, 1939.

† W. K. Lewis and A. H. Radasch, "Industrial Stoichiometry," McGraw-Hill Book Company, Inc., New York, 1926.

the chemical laws of combining weights. If gaseous materials are involved, for example, the relations between their masses, volumes, pressures, and temperatures (gas laws) must be employed. If a reaction can proceed in either direction, the laws of chemical equilibrium must be employed. If the rate at which a reaction proceeds is important, the laws of kinetics must be employed. We must therefore interpret the word "application" in a very broad sense also. It must be interpreted as permitting the use of any other physical and chemical laws that must be satisfied. This paints a broad picture indeed. One difficulty is that the scope of the field could logically be interpreted to include certain operations (such as distillation) and certain processes (such as hydrogenation) which are normally reserved for courses labeled "Unit Operations" and "Unit Processes." Unit operations and unit processes are logical extensions of the course in "industrial stoichiometry" or "industrial chemical calculations" (but their complexity warrants separate study); therefore no name can be proposed to substitute for "industrial stoichiometry" which is not subject to the above interpretation.

Now let us make our own position clear. We want to include in this text a certain amount of material on unit operations in order to give the embryo chemical engineer a feeling for the nature of his future work. In particular, we want to include mass and energy balances for some typical chemical-engineering equipment. We have chosen the title "Stoichiometry for Chemical Engineers" because it appears to us to defer to tradition while yet permitting the inclusion of the material on unit operations.

A course of this sort affords an excellent test of engineering aptitude and should be given in the sophomore year so that a student may change curricula if he finds that his aptitude does not equal his interest. It also affords an opportunity for the development of neat and logical work habits. These are particularly important in lengthy calculations, where a certain amount of bookkeeping skill is required. The mathematical and chemical principles involved form part of the foundation of the student's scientific knowledge. It is true that they may rightly be called "fundamental," but "fundamental" does not mean simple; it means basic. The principles may or may not be easy to comprehend. Comprehension of them can be facilitated by good teaching but will be ephemeral at best unless the student applies them in numerous problems. They are not to be memorized; they are to be learned.

Our objectives in writing this book are as follows:

1. To stress the use of fundamental principles, rather than reliance on memorized short cuts.

This objective is sometimes ignored in texts which are concerned with a relatively narrow field. For example, a book about combustion in furnaces, intended for people employed in the field, may well include

many clever short-cut methods of problem solution. These methods are unsuitable for undergraduates because they encourage memorization without comprehension.

2. To inculcate neat and logical habits of problem attack and problem-solution presentation.

This objective is an essential one in a calculations course. It is particularly important in this course because of the length and complexity of the problems.

3. To present a brief preview of chemical-engineering unit operations.

This objective is an integrating one. We believe that a sophomore should be earnestly inquiring into the scope and nature of his major discipline. We also believe that a preliminary course is appreciated best when its connection to that major discipline is illustrated. We feel that chemical-engineering students will be stimulated by this preview of their chosen field and that chemistry students, who may be concerned with obtaining the data with which chemical engineers work, will also be benefited.

The text is built around carefully chosen problems, which illustrate not only the principles of stoichiometry but also the particular calculation habits in which we are interested. Many practice problems are provided at the end of each section. A certain number of these have detailed solutions indicated in Appendix V, so that a student may check the form, as well as the substance, of his work.

This is a beginner's text. We have used relatively simple calculation methods so that emphasis will be upon the whole solution process rather than upon any one part of it. This is because we believe that the student must first learn to analyze a problem and to plan the solution and then learn to use refined methods of property prediction and refined mathematical techniques. After all, no amount of skill in the preparation of frosting will help a cook who cannot bake a cake.

Edwin T. Williams
R. Curtis Johnson

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Chapter 1

MATHEMATICAL PRINCIPLES

When you were a small child you were introduced to "pure" numbers in the first grade. You came home claiming that one plus one equals two and that two plus two equals four. When you were sturdily convinced of the verity and infallibility of these concepts and began to apply them by counting numbers of similar objects, your father swelled with pride and concluded that he had a bright little gaffer on his hands. However, when you innocently concluded, on the basis of pure-number theory, that one man equals one woman, your father realized that his little child still had a great deal to learn. This is an indication of a striking difference between pure and applied mathematics. In applied mathematics a number has a significance related not only to its magnitude but also to the quantity and substance to which it refers.

In this chapter we review the mathematical principles applied in this text and define some terms and establish some conventions that we shall follow.

DIMENSIONS, UNITS, LABELS, AND CONVERSION FACTORS

Physical systems, at rest or in motion, are commonly described by means of certain measurements. Primary quantities, such as length, mass, and time, are defined and used as the bases of measurement. Secondary quantities, such as density and viscosity, are then defined in terms of the primary quantities. The primary quantities are called *dimensions*. Units of measurement are defined for the dimensions according to the system of measurement. For example, the dimension *length* is expressed in the units *feet* in the English engineering (E.e.) system and in the units *centimeters* in the centimeter-gram-second (cgs) system. Table 1-1 gives the dimensions that we shall employ for our calculations and also gives the units in which the dimensions are expressed. Table 1-2 gives the dimensions and units of the secondary quantities that we shall use.

TABLE 1-1. PRIMARY QUANTITIES

Primary quantity (dimension)	Symbol	E.e. units	Cgs units
Mass	M	Pound mass (lb_m)	Gram mass
Force	F	Pound force* (lb_f)	Dyne†
Length	L	Foot	Centimeter
Time	θ	Hour or second	Second
Temperature difference	t or T	F° or R°	C° or K°
Heat	Q	British thermal unit (Btu)	Calorie

* The force exerted by gravity at sea level on a one-pound mass.

† The force necessary to give a one-gram mass an acceleration of 1 cm/sec^2.

TABLE 1-2. SECONDARY QUANTITIES

Quantity	Symbol	Dimensions	E.e. units	Cgs units
Density	ρ	M/L^3	lb_m/ft^3	g/cm^3
Specific volume	v	L^3/M	ft^3/lb_m	cm^3/g
Pressure	p, P	F/L^2	lb_f/ft^2	$dynes/cm^2$
Velocity	u	L/θ	ft/sec	cm/sec
Acceleration	a	L/θ^2	ft/sec^2	cm/sec^2
Viscosity	μ	$M/L\theta$	$lb_m/(ft)(sec)$	$g/(cm)(sec)$
Heat capacity	C	Q/Mt	$Btu/(lb_m)(F°)$	$cal/(g)(C°)$

Note the use of the symbols F° and C° in the heat-capacity row of Table 1-2. We employ this notation to distinguish a quantity which is a number of degrees from one which is a temperature. It serves to emphasize the fact that some phenomena depend on temperature difference, rather than on temperature level. This is not a general convention.

Following are some examples to illustrate the use of units.

Example 1-1. Kerosene costs 16¢/gal. How much does a quart of kerosene cost?

Solution

$$(1 \text{ qt})\left(\frac{16¢}{4 \text{ qt}}\right) = 4¢$$

or

$$(\tfrac{1}{4} \text{ gal})\left(\frac{16¢}{\text{gal}}\right) = 4¢$$

Example 1-2. Kerosene costs 16¢/gal. Gasoline costs 24¢/gal. What is the cost of 10 gal of gasoline?

Solution

$$(10 \text{ gal gasoline})\left(\frac{24¢}{\text{gal gasoline}}\right) = 240¢ \approx \$2.40$$

In Example 1-1 it was necessary to employ the same units of measure-

ment (called simply "units" in stoichiometry) to obtain a logical answer. In Example 1-2 it was necessary, in addition to using units, to use words (which we shall call "labels") which express the kind of material. Failure to use labels might lead to this "solution":

$$(10 \text{ gal})\left(\frac{16¢}{\text{gal}}\right) = 160¢ \approx \$1.60$$

The units cancel properly but the answer is incorrect because the unit "gallons" refers to different materials in the numerator and denominator.

Develop the habit of writing units and labels. You will find that cancellation of like quantities will lead to a completely expressed answer.

Example 1-1 could have been solved as follows:

$$(1 \text{ qt})\left(\frac{1 \text{ gal}}{4 \text{ qt}}\right)\left(\frac{16¢}{\text{gal}}\right) = 4¢$$

Note the use of the conversion factor 1 gal/4 qt. Conversion factors express the relations between the various units used to indicate a particular dimension. Since the numerator and the denominator of the conversion factor express equivalent quantities, multiplication by the factor does not change the quantity of material but merely the units in which that quantity is expressed.

A table of conversion factors is included in Appendix A. In the table we have listed common units and have indicated their equivalent in other units. When we give a conversion factor in the text we shall use an equivalence sign, i.e., 12 in. $\approx$ 1 ft. One should not write 12 in. = 1 ft because the equals sign refers specifically to numerical equality. Sometimes conversion factors are given by a statement such as this:

$$\text{in.} = (12)(\text{ft})$$

This statement is incomplete. It should be

$$\text{in.} = \left(\frac{12 \text{ in.}}{\text{ft}}\right)(\text{ft})$$

Pound Mass and Pound Force. Note the use of the terms "pound mass" and "pound force" in Tables 1-1 and 1-2. A pound force is, by definition, the force exerted on a pound mass by gravity at sea level at 45° latitude. In spite of the fact that mass and force are different concepts, it is ordinary engineering practice to refer to either a pound mass or a pound force as a pound. For example, density is given as lb/ft^3 and pressure as lb/ft^2 (refer to the proper notation in Table 1-2). The following treatment is intended to explain the relationship between the two pound units and also to show why the incorrect habit of using the same term for both does not always cause trouble.

The fundamental equation of motion is

$$\text{Force} = \alpha(\text{mass})(\text{acceleration})$$

where α is a constant the numerical value of which depends only on the units used. The acceleration of gravity at sea level and 45° latitude (called "standard" gravity) is 32.17 ft/sec². Therefore,

$$1 \text{ lb}_f = (1 \text{ lb}_m)\left(\frac{32.17 \text{ ft}}{\text{sec}^2}\right)$$

The value of α consistent with the use of "pound force" as the basic unit of force must be 1/32.17, and its units must be $(\text{lb}_f)(\text{sec}^2)/(\text{lb}_m)(\text{ft})$. The value 32.17 $(\text{lb}_m)(\text{ft})/(\text{lb}_f)(\text{sec}^2)$ is called g_c. We may give the same information as a conversion factor:

$$1 \text{ lb}_f \approx \frac{32.17 \ (\text{lb}_m)(\text{ft})}{\text{sec}^2}$$

Example 1-3. What is the potential energy (in ft-lb_f) of a 10-lb mass 6 ft above a certain datum plane anywhere on earth? The variation in gravity over the entire earth's surface rarely exceeds one-quarter of one per cent, so that the acceleration due to gravity, within the limits of engineering accuracy, is 32.17 ft/sec² anywhere on earth.

Solution

$$(6 \text{ ft})(10 \text{ lb}_m)\left(\frac{32.17 \text{ ft}}{\text{sec}^2}\right)\left(\frac{(\text{sec}^2)(\text{lb}_f)}{32.17 \ (\text{lb}_m)(\text{ft})}\right) = 60 \ (\text{ft})(\text{lb}_f)$$

Most engineers would solve the above problem as follows:

$$(6 \text{ ft})(10 \text{ lb}) = 60 \ (\text{ft})(\text{lb})$$

Some of them would not realize that the two pound units are different and that the above solution is true only because the mass is in a gravitational field that is essentially the same as the "standard" one upon which the definition of pound force is based. Another example of the same kind is as follows:

Example 1-4. What is the pressure (in lb_f/ft^2) exerted at the bottom of a 10-ft column of water (at 60°F) anywhere on earth by virtue only of the earth's attraction on the water (not including the pressure caused by the earth's atmosphere)?

Solution. The density of water at 60°F is 62.4 lb_m/ft^3.

$$(10 \text{ ft})\left(\frac{62.4 \text{ lb}_m}{\text{ft}^3}\right)\left(\frac{32.17 \text{ ft}}{\text{sec}^2}\right)\left(\frac{(\text{sec}^2)(\text{lb}_f)}{32.17 \ (\text{lb}_m)(\text{ft})}\right) = \frac{624 \text{ lb}_f}{\text{ft}^2}$$

Most engineers would write

$$(10 \text{ ft})\left(\frac{62.4 \text{ lb}}{\text{ft}^3}\right) = \frac{624 \text{ lb}}{\text{ft}^2}$$

and many of them would be unaware of the cancellation of g and g_c. If the column of water were on a planet with a gravitational acceleration of 720 ft/sec², the pressure would be

$$(10 \text{ ft})\left(\frac{62.4 \text{ lb}_m}{\text{ft}^3}\right)\left(\frac{720 \text{ ft}}{\text{sec}^2}\right)\left(\frac{(\text{sec}^2)(\text{lb}_f)}{32.17 \text{ (lb}_m)(\text{ft})}\right) = \frac{13{,}980 \text{ lb}_f}{\text{ft}^2}$$

The final example is one in which no fortuitous cancellation can occur because the gravitational field has nothing to do with the phenomenon.

Example 1-5. A moving mass has a certain amount of energy (called *kinetic energy*) because of its motion. At speeds usually encountered in engineering work, this energy is given by the following equation:

$$\text{KE} = \tfrac{1}{2}mv^2$$

What is the kinetic energy (in ft-lb$_f$) of a 6-lb mass at the instant when it is moving with a velocity of 10 ft/sec?

Solution

$$\text{KE} = \left(\frac{1}{2}\right)(6 \text{ lb}_m)\left(\frac{100 \text{ ft}^2}{\text{sec}^2}\right)\left(\frac{(\text{sec}^2)(\text{lb}_f)}{32.17 \text{ (lb}_m)(\text{ft})}\right) = 9.33 \text{ (ft)(lb}_f)$$

Note that gravity is not involved. The 32.17 is simply a conversion factor which replaces the units (lb$_m$)(ft)/sec² by the unit lb$_f$. It is the defined constant g_c. Engineering texts often express kinetic energy as $\frac{1}{2}mv^2/g_c$ to be sure that the conversion factor will appear in the calculation.

Ratios and Fractions. The significance of a given or calculated quantity in stoichiometry often depends not only upon its magnitude but also upon its relative magnitude with respect to other quantities. The relative magnitude may be expressed by the use of ratios or fractions. A ratio denotes the proportion between one quantity and another. A fraction is a ratio signifying the proportion of a larger quantity which the quantity in question represents.

Fractions may be expressed in per cent, or parts per hundred. Note that fractions (whether expressed as per cent or not) and ratios have units and labels.

CHEMICAL ANALYSES

Analyses may be given on one of several bases, depending on the state of the material being analyzed. Unless otherwise stated, the analysis of solids is on a weight basis. A coal containing 65% carbon has 65 lb of carbon in every 100 lb of coal.

A liquid analysis may be stated on either a weight or a mole basis.

Usually the compositions of solutions of solids in liquid are reported in weight per cent.

The analyses of gaseous mixtures are reported on a mole or volume basis. For perfect-gas mixtures, as explained later, these analyses are identical.

In this book we shall employ the symbols %m, %w, and %v to signify percentage by moles, weight, and volume.

Example 1-6. A salt solution originally 4%w NaCl in water is evaporated until the concentration is 5%w NaCl.

a. What percentage of the water in the original solution is evaporated?

b. What is the percentage reduction in the weight of the original solution?

Solution

Basis: 100 lb of the 4%w solution. (*Note:* It is necessary to pick a basis for calculation. It is desirable to state what the basis is. The choice should not be made arbitrarily but after careful thought, since the difficulty of the calculations may depend upon the basis chosen.)

Evaporation can remove only water, since NaCl is not volatile. Therefore all the salt originally present will be present in the final solution.

This fact is the key to the solution of the problem.

a. Percentage of water evaporated

$$\left(\frac{0.04 \text{ lb NaCl}}{\text{lb orig soln}}\right)(100 \text{ lb orig soln}) = \left(\frac{0.05 \text{ lb NaCl}}{\text{lb final soln}}\right)(X)$$

where X = lb final soln. $X = 80$ lb.

$$100 \text{ lb (orig soln)} - 80 \text{ lb (final soln)} = 20 \text{ lb } H_2O \text{ evap}$$

$$\frac{20 \text{ lb } H_2O \text{ evap}}{96 \text{ lb } H_2O \text{ orig present}} = \frac{0.208 \text{ lb } H_2O \text{ evap}}{\text{lb } H_2O \text{ orig present}}$$

$$(0.208)(100) = 20.8\%$$

b. Percentage of original solution evaporated

$$\left(\frac{20 \text{ lb } H_2O \text{ evap}}{100 \text{ lb orig soln}}\right)(100) = 20\%$$

This problem could also have been solved as follows:

Basis: 1 lb NaCl

$$\frac{96 \text{ lb } H_2O}{4 \text{ lb NaCl}} - \frac{95 \text{ lb } H_2O}{5 \text{ lb NaCl}} = \frac{5 \text{ lb } H_2O \text{ evap}}{\text{lb NaCl}}$$

Basis: 100 lb 4%w solution, or 4 lb NaCl

$$\left(\frac{5 \text{ lb } H_2O \text{ evap}}{\text{lb NaCl}}\right)(4 \text{ lb NaCl}) = 20 \text{ lb } H_2O \text{ evap, etc.}$$

The first method of solution shows the use of fractions (with proper units and labels). In the second method the solution was accomplished by the use of ratios. You see that the relationships between the constituents of a mixture may be expressed in various ways. For instance, knowing that the original solution is 4%w salt in water tells us that there are 4 lb NaCl/100 lb soln, 4 lb NaCl/96 lb H_2O, 96 lb H_2O/100 lb soln, 100 lb soln/4 lb NaCl, 96 lb H_2O/4 lb NaCl, and 100 lb soln/96 lb H_2O. The recognition of these relationships is important. Selection of the proper one can simplify the solution of a particular problem.

Example 1-6 might also have been solved as follows:

Basis: 100 lb original (4%w) solution. Let X = amount of H_2O evaporated.

$$96 - X = \text{lb of } H_2O \text{ remaining}$$

$$96 - X = \left(\frac{0.95 \text{ lb } H_2O}{\text{lb final soln}}\right)(Y) \tag{1-1}$$

where Y = lb final soln.

$$X + Y = 100 \tag{1-2}$$

Substituting Eq. (1-2) in (1-1), we obtain

$$96 - X = (0.95)(100 - X)$$

and $X = 20$ lb H_2O evaporated, etc.

The above calculation is much less straightforward than the previous calculations, which took direct cognizance of the fact that the amount of salt in solution was unchanged by the process. It is good practice to choose a compound or a material which goes through the process unchanged and to use it as the "key" to relate the streams of material. This is not always possible. We shall reserve a discussion of other possibilities for Chap. 3. The practice problems at the end of this and the next chapter will give you an opportunity to form some opinions on this subject for yourself before you read the more detailed discussions in Chap. 3. Remember that the "brute-force" method illustrated above is always possible. Simply write a multiplicity of independent material balances on compounds or elements until you have enough equations to solve for all the unknown quantities.

Since percentage values are fractions, they cannot be added or subtracted unless they have a common denominator, or basis. The original solution in the example was said to contain 4%w NaCl. The basis for this figure is 100 lb of original solution. We may write the fraction 4 lb NaCl/100 lb orig soln. An example of a common error is

96%w H_2O in orig soln − 95%w H_2O in final soln = 1%w H_2O evap

Since this calculation has absolutely no meaning, there is no "reason" for the next step in the calculation which is usually to multiply the weight

of the original solution by 1% to find the pounds of water evaporated. If the percentages are written as fractions with the bases shown, the fallacy of the above operation is clear:

$$\frac{96 \text{ lb } H_2O}{100 \text{ lb orig soln}} - \frac{95 \text{ lb } H_2O}{100 \text{ lb final soln}} = ?$$

The basis for a percentage value is not always obvious. For instance, the moisture content of many solid materials (coal, paper, plywood, etc.) is expressed as a percentage of the dry solid rather than as a percentage of the moist solid. Whenever there is a possibility of confusion, the basis should be stated.

Example 1-7. Paper is passing continuously through a tunnel drier. The entering paper contains 10%w H_2O (dry basis, i.e., 10 lb H_2O/100 lb dry paper), and the leaving paper contains 2%w H_2O (dry basis). How many pounds of water is evaporated per hour if 1000 lb/hr of paper enters the drier?

Solution

Basis: 1 hr of operation

$$\left(\frac{1000 \text{ lb "entering paper"}}{\text{hr}}\right)\left(\frac{100 \text{ lb dry paper}}{(100 + 10) \text{ lb "entering paper"}}\right) = \frac{909 \text{ lb dry paper entering}}{\text{hr}}$$

$$\left(\frac{909 \text{ lb dry paper}}{\text{hr}}\right)\left(\frac{0.1 \text{ lb } H_2O}{\text{lb dry paper}} - \frac{0.02 \text{ lb } H_2O}{\text{lb dry paper}}\right) = \frac{72.72 \text{ lb } H_2O \text{ evap}}{\text{hr}}$$

Example 1-8. Change the moisture contents of Example 1-7 to the wet basis and do the problem again.

Solution

$$\left(\frac{10 \text{ lb } H_2O}{(100 + 10) \text{ lb "entering paper"}}\right)(100) = 9.09\%\text{w } H_2O \text{ (wet basis) entering}$$

$$\left(\frac{2 \text{ lb } H_2O}{102 \text{ lb "leaving paper"}}\right)(100) = 1.96\%\text{w } H_2O \text{ (wet basis) leaving}$$

Basis: 1 hr of operation

$$\left(\frac{1000 \text{ lb "entering paper"}}{\text{hr}}\right)\left(\frac{9.09 \text{ lb } H_2O}{100 \text{ lb "entering paper"}}\right) = \frac{90.9 \text{ lb } H_2O \text{ entering}}{\text{hr}}$$

$$\text{Therefore,} \qquad 1000 - 90.9 = \frac{909.1 \text{ lb dry paper entering}}{\text{hr}}$$

$$\left(\frac{909.1 \text{ lb dry paper leaving}}{\text{hr}}\right)\left(\frac{1.96 \text{ lb } H_2O}{98.04 \text{ lb dry paper}}\right) = \frac{18.18 \text{ lb } H_2O \text{ leaving}}{\text{hr}}$$

$$90.9 - 18.18 = \frac{72.72 \text{ lb } H_2O \text{ evap}}{\text{hr}}$$

A comparison of this solution with that of Example 1-7 shows why analyses are commonly reported on a dry basis in certain industrial processes. In this text we shall state whenever the analysis of a solid is reported on a dry basis.

Procedure. Logical procedure and neat presentation facilitate the solution of problems in stoichiometry. Logical procedure helps to prevent the calculation of unnecessary quantities. Neat and complete presentation avoids careless errors and makes the solution easier to read and understand. Following is a suggested procedure:

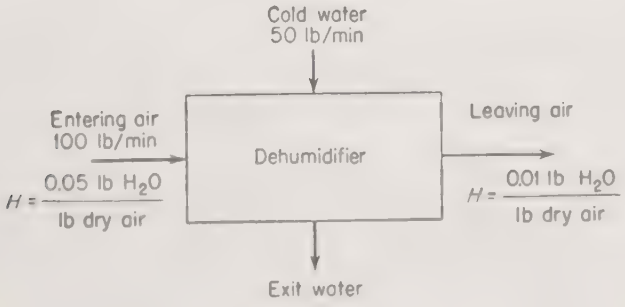
1. Read the entire problem carefully.
2. Draw a diagram, labeling it thoroughly.
3. Plan the solution. If the problem is long, make a brief outline of the steps in the calculation. Be sure to look for "key" materials, and be sure to state the basis for each calculation.
4. Proceed with the solution, writing all chemical equations involved and employing units and labels.
5. Check the answer qualitatively (see Qualitative Considerations).

Example 1-9. A dehumidifier sprays 50 lb of cold water per minute into a stream of air. One hundred pounds of wet air per minute enters the dehumidifying chamber. The absolute humidity of the entering air is 0.05 lb H_2O/lb dry air, and that of the leaving air is 0.01 lb H_2O/lb dry air.

a. What is the total weight of liquid water leaving the dehumidifier per minute?

b. What is the weight of wet air leaving per minute?

Solution



Basis: 1 min. All the constituents of the entering "wet-air" stream are gases. Water vapor is the only gas in the entering stream which can be condensed by a cold-water spray. Some of it is condensed and leaves as liquid water. The rest of it leaves in the vapor state. (*Vapor* is the term applied to a gas which is easy to condense.) The other constituents of the "wet-air" stream, i.e., the "dry air," remain in the gaseous state. This means that the dry air can serve as a key component to relate the entering and leaving wet-air streams.

$$(100 \text{ lb entering wet air})\left(\frac{1 \text{ lb dry air}}{1.05 \text{ lb wet air}}\right) = 95.2 \text{ lb dry air entering (and leaving)}$$

Since we can calculate the amount of water condensed per pound of dry air, we can calculate the total water condensed in 1 min.

Basis: 1 lb of dry air

$$\frac{0.05 \text{ lb water vapor entering}}{\text{lb dry air}} - \frac{0.01 \text{ lb water vapor leaving}}{\text{lb dry air}} = \frac{0.04 \text{ lb } H_2O \text{ condensed}}{\text{lb dry air}}$$

Basis: 1 min

$$(95.2 \text{ lb dry air})\left(\frac{0.04 \text{ lb } H_2O \text{ condensed}}{\text{lb dry air}}\right) = 3.81 \text{ lb } H_2O \text{ condensed}$$

a. Weight of liquid water leaving

50 lb liquid H_2O entering + 3.81 lb H_2O condensed = 53.81 lb

b. Weight of wet air leaving

$$(95.2 \text{ lb dry air})\left(\frac{1.01 \text{ lb wet air}}{\text{lb dry air}}\right) = 96.2 \text{ lb wet air}$$

or

100 lb entering wet air − 3.81 lb H_2O condensed = 96.2 lb leaving wet air

In drawing a diagram for a problem it is sufficient to use labeled boxes to represent pieces of equipment. The actual mechanisms by which the reactions or transformations take place are of no importance; we are concerned only with the materials which enter and those which leave. These entering and leaving streams of material are customarily indicated by arrows.

If the streams are carefully labeled and the conditions (temperature, pressure, etc.) noted, the diagram has served to change a word description of the problem into a pictorial representation. It is easy to refer to such a diagram for information.

The dry air serves as the "key" component. A basis of 1 min is chosen because the answers are required on that basis. Note that all streams must be related by putting them on the same basis. We could not add the sprayed water to the condensed water if they were not related by a common basis.

Qualitative Considerations. Errors in arithmetic or reasoning can often be recognized by a qualitative consideration of each quantity calculated. In Example 1-9, if the amount of wet air leaving the dehumidifier per minute had been calculated as 101 lb, we should have known the answer was impossible, since only 100 lb of wet air entered and some of the water vapor was removed.

Ask yourself, about each answer, "Is it larger or smaller, hotter or colder, faster or slower?" or some other qualitative question, in order to be sure that the answer bears a reasonable relationship to the other quantities in the problem.

Techniques. While many engineers do little with formal mathematics, they do perform endless calculations. There is generally a "best" way to solve a problem. We shall frequently illustrate one of these "best" ways. The use of legitimate short cuts, graphical aids, and "educated guesses" frequently shortens long tedious calculations and turns long and dull problems into new and interesting challenges.

Practically every problem in this text requires that an equation be set up to find something, this something being a numerical value of a rate, time, volume, composition, pressure, or other physical or chemical variable. In most cases more than one question will have to be answered. Sometimes the other quantities to be found are merely intermediates with no interest except that they must be found to determine the final answer. The most common method of expressing a word statement in mathematical form is by means of an algebraic equation. When we know the value of something, we write down that number; when we do not know the value, we choose some letter (usually x as a matter of custom). Then x takes on the significance of "What?" If we have two variables, we may label the second one y and think of y as "What else?"

Suppose that we analyze an equation

$$x + y = 50{,}000$$

This asks, What plus what else equals 50,000? The question is rather ridiculous. We could choose any value of x and find a value of y which would be satisfactory.

Suppose that, instead, we write two equations

$$x + y = 50{,}000$$

and

$$0.50x + 0.25y = 15{,}000$$

We might express this as What plus what else equals 50,000, if one-half of the same "what" plus one-fourth of the same "what else" equals 15,000? This begins to make sense, and we find that only one set of answers applies, that is, $x = 10{,}000$ and $y = 40{,}000$. Thus we have illustrated one very important principle; we must have as many equations as unknowns to be able to solve for all the unknowns.

We see that it is relatively easy to make word statements from equations. We merely substitute "What?" for x, "What else?" for y, and other different word combinations for any other variables which may be present. The engineer, however, must start with a word situation and then write the equations.

Example 1-10. A company receives a shipment of 50,000 lb of two chemicals, A and B. The total cost, excluding shipping charges, is \$15,000. The price of A is 50¢/lb; the price of B is 25¢/lb. How many pounds of A and B were shipped?

Solution. We see that there are two unknowns, the pounds of A and the pounds of B. Let x denote the former, y the latter. The total shipment equals 50,000 lb, and so we write

$$x + y = 50{,}000$$

The total cost of A is (0.50 \$/lb)(x lb), and the total cost of B is (0.25 \$/lb)(y lb). The sum must equal \$15,000, and so we write

$$0.50x + 0.25y = 15{,}000$$

Is the problem now any different from the straight mathematical problem presented earlier?

There is one difference which is not apparent from the equations, and that is that the values of x and y must both fall between 0 and 50,000. Suppose that the problem had been stated as above except that the total cost was given as \$10,000. The proper equations would be

$$\begin{aligned} x + y &= 50{,}000 \\ 0.50x + 0.25y &= 10{,}000 \end{aligned}$$

The correct solution to these equations is $x = -10{,}000$, $y = 60{,}000$. Because of the added limitation, however, we see that the data must be wrong.

Average and Mean. The words "mean" and "average" have been misused so much that the meaning intended by a particular author may not be clear. In this text we are concerned with the arithmetic average and the arithmetic mean. They are normally referred to simply as "the average" or "the mean." There are other kinds of averages (and means).

An arithmetic average is merely the sum of a number of values divided by that number. Thus the average grade in a class where the individual

grades are 55, 63, 72, 73, 86, and 91 is $44\frac{9}{6}$ or $73\frac{1}{3}$. Averages are usually taken of "discrete" quantities, such as grades, incomes, etc.

Example 1-11. The prices of the five best-selling automobiles in a certain area are \$2470, \$2580, \$2620, \$2900, and \$3150. What is the average price paid for an automobile in this area?

Solution. If we average the five values as before, the average price appears to be \$2744. Suppose that we collect further statistics as follows:

Model	Price, \$	Number sold
A	2470	502
B	2580	556
C	2620	460
D	2900	320
E	3150	289

Now let us take a "weighted average." Each price is multiplied by the number of that model sold, and the sum divided by the total number sold. We then find the average price paid to be

$$\frac{5{,}717{,}970}{2127} = \$2688.28$$

This figure would certainly be more indicative of the cash that the average purchaser is willing to spend for an automobile. Note that we are still averaging "discrete" values but that a little judgment has indicated that certain figures are "worth more" than others in the averaging process.

When we consider smooth (or continuous, or nondiscrete) variables, the weighted average may be obtained by integration; thus if y is a function of x, the mean value of y, $\bar{y}$, is given by

$$\bar{y} = \frac{\int_{x_1}^{x_2} y\,dx}{\int_{x_1}^{x_2} dx}$$

Since the definite integral of dx is merely $x_2 - x_1$, we may write

$$(\bar{y})(x_2 - x_1) = \int_{x_1}^{x_2} y\,dx$$

The average obtained by integration is called the *integrated average* or *mean*. In this case it is an arithmetic mean. If one were dealing with a geometric average of discrete variables, a similar average obtained by integration for continuous variables would be termed the *geometric mean*, and the same is true for other kinds of averages.

Graphical and Numerical Methods. Graphical methods for the solu-

tion of algebraic systems are of particular interest to engineers, who frequently do not need an answer as precise as that obtainable by an analytical solution. Even when a precise answer is required, an engineer may prefer to do a graphical solution to get an approximate answer which he may refine by the numerical methods discussed later.

Even the solution of a simple, obvious equation has a graphical, or geometric, significance. Suppose that we have

$$x + y = 50{,}000$$

and suppose that the value of y is known to be 40,000. We now write

$$x + 40{,}000 = 50{,}000$$

Even though the answer, 10,000, is obvious, let us explore some indirect methods of getting the answer which will become important in problems where the answer is not so obvious.

Set $$x + 40{,}000 = z = 50{,}000$$

and plot the two equations (see Fig. 1-1)

$$x + 40{,}000 = z$$

and $$z = 50{,}000$$

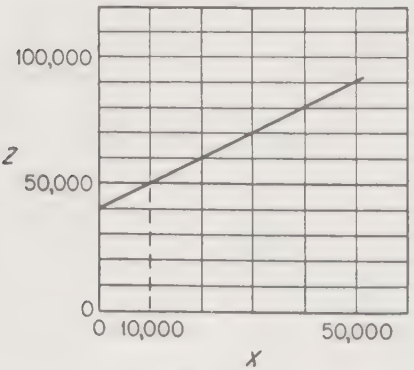


Fig. 1-1

The two intersect at the known answer of 10,000. While the method is trivial here, consider this example:

Example 1-12. Oxygen has a heat capacity C_p, in cal/(g mole)(K°), which is a function of absolute temperature T, in °K, represented by the equation

$$C_p = 8.27 + 0.000258T - \frac{187{,}800}{T^2} \tag{1-3}$$

At what temperature is the heat capacity equal to 8.44?

Solution. For the moment, we need not be concerned with the exact meaning of the heat capacity. We may first try an analytical solution. When we set $C_p = 8.44$, and multiply the equation by T^2, we find

$$0.000258T^3 - 0.17T^2 - 187{,}800 = 0 \tag{1-4}$$

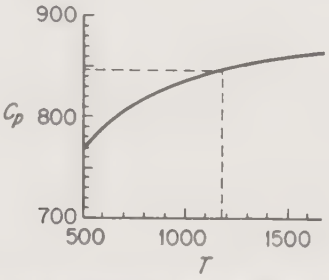
Certainly no mathematical solution is immediately apparent. This is a cubic equation, and there may be three real roots (or there may be only one real root and two imaginary roots).

Instead of attempting an analytical solution, we may calculate the

heat capacities at some selected temperatures and plot them vs. temperature to find the answer. We first calculate a few values from Eq. (1-3).

T	500	1000	1500
C_p	7.65	8.34	8.57

This should represent the region of interest, since some of the values are below the desired answer and one is above. We proceed to make the plot and from this read off a value of 1200 as an approximate answer.



As a check we might now calculate the heat capacity at 1200°. The calculation shows 8.45. Taking a slightly lower value of 1180° gives us the desired answer.

Numerical methods, often called "trial and error," are useful when an analytical solution would be difficult. To solve Example 1-12 we could have proceeded as follows:

Rearrange Eq. (1-4).

$$T = \frac{0.17}{0.000258} + \frac{187{,}800}{0.000258T^2} \tag{1-5}$$

or

$$T = 658.9 + \frac{7.275 \times 10^8}{T^2}$$

Assume various values for T to substitute in the T^2 term, and calculate the T on the left side of the equation.

Assumed T	Calculated T	Assumed T − Calculated T
800	1797	−997
1000	1386	−386
1200	1164	+ 36
1400	1030	370
1600	943	657

We may now make one of two types of plot. The first is the calculated vs. the assumed value (Fig. 1-2). An answer is obtained when the two agree, or cross the diagonal line on the diagram. The second is the

difference vs. the assumed value (Fig. 1-3). An answer is obtained when the difference is zero.

One method is fundamentally as good as the other; certain problems may dictate one or the other as preferable.

There is another numerical method, known as *iteration*, for solving problems of this type. It is generally successful, although certain problems may "blow up" if bad initial assumptions are made. In this

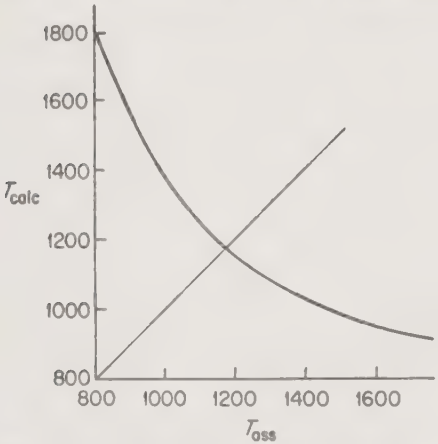


FIG. 1-2. Comparison of assumed and calculated values.

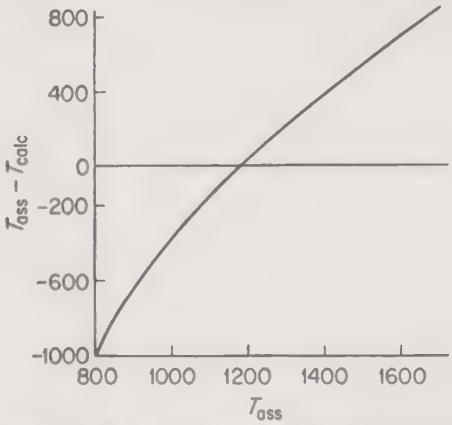


FIG. 1-3. Difference between assumed and calculated values vs. assumed values.

method we select an initial value to try. This value is substituted for the unknown in all parts of the equation except for one term. The value is then calculated and used as the next trial value. The procedure continues until satisfactory agreement between assumed and calculated values is obtained.

In this problem we will substitute trial values in the T^2 term of Eq. (1-5), calculate T, and use this value as the next trial. The results of the calculation are shown in the table on page 17.

You can see that the values have been slowly converging on the known answer of 1180°. However, in this case (and this is the unpredictable part of iterative calculations) the convergence is very slow. Some method might be found to speed up the process. Suppose we start over, and use the average of the assumed and calculated temperatures for the next trial.

Trial	Assumed T	Calculated T
1	800	1797
2	1298.5	1090.4
3	1194.5	1168.8
4	1181.7	1179.9
5	1180.8	1180.7

In this case, the answer was obtained in only five trials. By using a bit of common sense, based on observation of performance of the numbers calculated, we found a much better method of calculation.

Trial	Assumed T	Calculated T
1	800	1797
2	1797	884.2
3	884.2	1589.5
4	1589.5	946.9
5	946.9	1470.3
6	1470.3	995.4
7	995.4	1393.2
8	1393.2	1033.7
9	1033.7	1339.8
10	1339.8	1064.2
11	1064.2	1301.3
12	1301.3	1088.5
13	1088.5	1272.9
14	1272.9	1107.9
15	1107.9	1251.6
16	1251.6	1123.3
17	1123.3	1235.5
18	1235.5	1135.5
19	1135.5	1223.1
20	1223.1	1145.2
21	1145.2	1213.8
22	1213.8	

In performing iterative calculations, it is a good idea to make a "running plot" as the calculation proceeds. Any suitable plot, such as calculated vs. assumed value, difference vs. assumed value, or calculated value vs. trial number, might be satisfactory.

As an exercise, demonstrate that the iterative process for calculating square roots is valid, using the equation

$$a_{n+1} = \left(\frac{b}{a_n} + a_n\right)\left(\frac{1}{2}\right)$$

where b = number whose square root is desired
a_n = trial value of square root
a_{n+1} = next trial value

Try the process for known numbers, such as $b = 256$, using any positive value for a_0, the first trial value.

There are graphical and numerical techniques associated with simple

calculus as well as with algebra. Suppose that we consider two problems which may appear similar at first but which differ fundamentally.

Example 1-13. Coal is weighed as it enters a furnace. The following readings are taken of the weight of each load:

Time, hr	0	1	2	3	4	5	6
Coal added, lb	150	154	156	150	130	90	50

What is the total amount of coal added and the average amount used per hour?

Solution. If we exclude the first reading and consider the coal added to maintain the furnace after the first hour, we merely add the figures (excluding 150) and arrive at 730 lb as the total used over a 6-hr period. The average rate of use is 121.7 lb/hr. If we can assume that coal was fired exactly 1 hr before the first reading, so that the first value of 150 is representative, we might add it in and say that 880 lb was used in 7 hr, giving a higher rate of 125.7 lb/hr. Note that, to find the total amount, when we are working with discrete readings of amounts added in lump sums, we merely added the figures.

Example 1-14. A chemical is being metered to a process. Readings of the *rate of addition* are taken hourly. The readings are exactly the same as in the previous example. What is the total amount of chemical added in 6 hr?

Solution. Here we find that we do not know total amounts added in discrete increments. Instead we have merely spot readings of the rates as functions of time. If we let W equal the total amount that has been added to the process and R be the rate at which addition takes place, we find, by definition, that

$$\frac{dW}{d\theta} = R$$

where θ = time, in this case hr. Thus, to find the total amount added to the process, we must perform an integration:

$$W_n - W_0 = \int_{\theta_0}^{\theta_n} R \, d\theta$$

where 0 represents the start of the process and n the final condition.

To perform the integration, we look for a convenient explicit expression which relates R and θ, that is, which expresses R in terms of θ. Such can be found in some cases by more advanced techniques. However, there are three methods not requiring more advanced techniques which are extremely useful. Two are numerical methods; the third is graphical.

The most common numerical method, which can be used when functions do not vary too erratically, is the trapezoid rule. We give here

only the formula and the solution to the problem, expecting you to review the rule in your calculus text.

$$W_n - W_0 = (\tfrac{1}{2})(R_0 + 2R_1 + \cdots + 2R_{n-1} + R_n)\,\Delta\theta$$

where the R's are the rate readings and $\Delta\theta$ the time increment between readings. Numerically,

$$W_n - W_0 = W_6 - W_0 = (\tfrac{1}{2})[150 + 2(154) + 2(156) + 2(150) + 2(130) + 2(90) + 50](1) = 780 \text{ lb} \quad \text{or} \quad \frac{130 \text{ lb}}{\text{hr}} \text{ average}$$

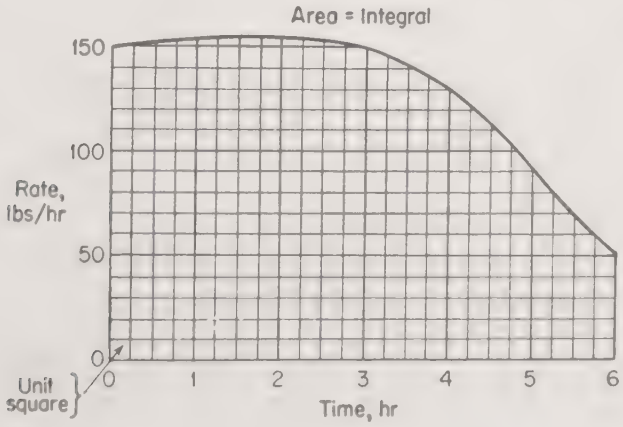
The next most common numerical method is Simpson's rule, which you should also review. In this case, an odd number of readings must be available. Then,

$$W_n - W_0 = \tfrac{1}{3}(R_0 + 4R_1 + 2R_2 + 4R_3 + 2R_4 + \cdots + 2R_{n-2} + 4R_{n-1} + R_n)\,\Delta\theta$$

where again $\Delta\theta$ is the time increment. Numerically,

$$W_6 - W_0 = (\tfrac{1}{3})[150 + 4(154) + 2(156) + 4(150) + 2(130) + 4(90) + 50](1) = 782.7 \text{ lb} \quad \text{or} \quad \frac{130.5 \text{ lb}}{\text{hr}}$$

The graphical method is called *graphical integration.* It is based on the fact that the integral of $R\,d\theta$ may be looked upon as an area, even when it has no physical significance as an area. If we plot R vs. θ and count the squares under the curve between the value $R = 0$ and the curve, we then multiply the number of squares by the value of a unit square, to obtain the answer.



$$\text{Value of unit square} = \left(\frac{10 \text{ lb}}{\text{hr}}\right)(0.25 \text{ hr}) = 2.5 \text{ lb}$$

$$\text{Number of squares} = 310$$

$$W = \text{total lb} = (310)(2.5) = 775 \text{ lb}$$

and

$$\text{Average rate} = \frac{129.7 \text{ lb}}{\text{hr}}$$

Chemical-plant data do not usually follow smooth curves. Most evaluations of equipment performance must be made by just such methods as these.

Note one other point in our calculations. In determining the "average" rate, we have actually used the theorem of the mean and obtained the so-called "integrated average."

Beginning students are usually loath to attempt graphical or "trial and error" solutions. You might gain a better appreciation of their value by attempting an analytical solution of the following problem before solving it graphically or by trial and error.

The bottom of a 30-ft ladder is pressed against the bottom of a wall which faces east, and the ladder leans against a wall which faces west. A 40-ft ladder leans against the wall which faces east, and its bottom is at the bottom of the wall which faces west. The ladders cross at a point 10 ft above the ground. How far apart are the two walls?

PROBLEMS

1-1. Using only the factors 1 ft $\approx$ 12 in., 1 in. $\approx$ 2.54 cm, and 1 liter $\approx$ 1000 cm^3, find the number of liters in 1 ft^3.

1-2. Using the factors 1 lb $\approx$ 454 g and 1 ton $\approx$ 2000 lb, calculate the number of tons in 1000 kg.

1-3. Density is always expressed as mass per unit volume. If an organic liquid has a density of 0.9 g/cm^3, and 1 ft^3 $\approx$ 7.481 gal, how many cubic feet are needed to hold 1000 lb of the liquid? How many gallons?

1-4. Specific gravity is the ratio of the density of a substance to that of a reference substance. It is a dimensionless number. Since density changes with temperature, the temperatures of both substances must be given. Water at 4°C is often used as a reference substance. Its density is 1.0000000 g/cm^3.

The density of benzene at 15°C is 0.7896 g/cm^3. What is its specific gravity relative to water at 4°C?

What is the density at 30°C of a liquid whose specific gravity at 30°C relative to water at 4°C is 1.2061? State the answer in g/cm^3 and lb/ft^3.

1-5. Convert a velocity of 60 miles/hr to m/sec.

1-6. Convert an acceleration of 10 ft/sec^2 to miles/hr^2.

1-7. Convert a rate of flow of 1 liter/hr to gal/min.

1-8. Convert a mass rate of flow of 10 lb/(ft^2)(min) to kg/(m^2)(sec).

1-9. Unless of a special form, all equations must be dimensionally consistent; i.e., each term must have the same dimensions as all other terms. Densities may some-

times be expressed as linear functions of temperature, such as

$$\rho = \rho_0 + At$$

where ρ = lb/ft³ at temperature t
ρ_0 = lb/ft³ at temperature t_0
t = temperature, °F

What must the units of A be?

1-10. In fluid flow the Reynolds number is dimensionless.

$$\text{Re} = \frac{Du\rho}{\mu}$$

where D = diameter
u = velocity
ρ = density
μ = viscosity

If D is in feet, u in ft/sec, and ρ in lb/ft³ (standard English units), what are the units of μ?

1-11. An operator in a chemical plant has instructions to see that a salt is added continuously to a stream of salt-free solvent at such a rate that the resulting mixture is 20%w salt.

a. If the outlet composition in %w is twice the desired value, what is the ratio of the amount of salt the operator added to the amount that he should have added?

b. If he used twice as much salt as he should, what would the outlet concentration be?

1-12. A solution contains 25%w salt in water.

a. Express the composition as pounds salt/pound water, pounds water/pound salt, and %w water.

b. What is the composition, in %w salt, if 40% of the water originally present is evaporated?

c. What is the composition if an amount of water equal to 40% of the weight of the original solution is evaporated?

d. How much water must be evaporated from 100 lb of the solution if its final composition is to be 40%w H_2O?

1-13. It is desired to make up 100 lb of a solution containing 35%w salt. Two solutions are available, one containing 10%w salt and the other containing 50%w salt. How many pounds of each solution will be required?

1-14. Two identical samples of wet coal are given to two analysts. One reports this analysis in %w: 75% C, 4% H, 8% O, 2% N, 1% S, and 10% ash. The other dries his sample first and finds that it loses moisture equal to 7% of its weight. He then reports an analysis of the dried coal, also on a %w basis. What should his analysis be? (Hydrogen and oxygen are combined in water in a weight ratio of 1:8.)

1-15. A saturated solution of a salt is made by agitating an excess of the salt in water and then draining off the solution. When this is done, a certain quantity of solution always remains adsorbed on the undissolved salt. If 1 lb of water will dissolve 0.2 lb of a salt and if 0.5 lb of solution will remain adsorbed on 1 lb of undissolved salt,

a. How much solution can be drained off when 1000 lb of water is mixed with 500 lb of salt?

b. If the remaining wet salt were thoroughly dried, how much dry salt would be obtained?

1-16. At 0°C a water solution of 23.5 g of common salt in 100 cm³ of solution has a density of 1.16 g/cm³.

a. What is the composition of the solution in %w salt?

b. How many pounds of salt would be dissolved in 1 ft^3 of solution?

1-17. A wet slurry of talc in water contains 75% H_2O by weight. Eighty per cent of the water is removed by filtration and drying, which reduces the weight of material left by 600 lb.

a. What is the original weight of the slurry?

b. What is the water content of the concentrated slurry after filtration and drying?

1-18. A company uses a certain chemical in 20%w solution in water in one of its manufacturing processes. A long-term contract for purchase of large quantities of the chemical is made with a supplier. The contract sets a price of \$0.50/lb for a 50%w solution, with provision for price adjustment if the concentration is different. A shipment of 10 tons is analyzed and found to be 45%w. Freight and handling costs, paid directly to the carrier, amount to \$0.10/lb. The supplier submits a bill for \$9000. Is this bill correct?

1-19. The vapor evolved when a mixture of liquids is heated is usually of a different composition than the original mixture. One hundred kilograms of a mixture consisting of 60%w of liquid *A* and 40%w of liquid *B* is heated and some vapor is removed. After the process the remaining liquid contains 10% *A* and the vapor contains 80% *A*.

a. What is the sum of the weights of the vapor and the remaining liquid?

b. What is the sum of the weights of *A* in the vapor and in the remaining liquid?

c. What is the sum of the weights of *B* in the vapor and in the remaining liquid?

d. What are the weights of the vapor and the remaining liquid?

e. What percentage of the *A* originally present is in the vapor?

1-20. A crude salt, when dissolved in water, yields a brine whose composition is 20%w NaCl, 0.5% NaBr, 2% $MgCl_2$, and 77.5% H_2O. Some of the water is evaporated. At the same time, 50% of the NaCl originally present is crystallized out in pure form. The concentrated solution remaining weighs 30% as much as the initial brine. When 100 lb of brine is thus treated,

a. What is the sum of the weights of evaporated water, crystallized NaCl, and concentrated solution?

b. What is the sum of the weights of NaCl in the solution and crystals?

c. What is the weight of the $MgCl_2$ in the concentrate?

d. What is the weight of the NaBr in the concentrate?

e. What is the weight of water in the concentrate and evaporated water?

f. What are the weights of NaCl precipitated, water evaporated, and concentrate?

g. What percentage of the water originally present is evaporated?

h. If all the water were removed from the concentrate, what would be the composition of the remaining mixed salts?

1-21. A plant for the production of NaOH concentrates a solution of 10%w NaOH, 10% NaCl, and 80% H_2O by evaporation. During evaporation some NaCl crystallizes out pure. If the final solution contains 50% NaOH and 1% NaCl, calculate the following:

a. The pounds of water evaporated per ton of initial solution

b. The pounds of NaCl precipitated per ton of initial solution

c. The weight of the final solution

1-22. You have been given the problem of making a liquid mixture consisting of 1 part *A*, 1.5 parts *B*, and 2.5 parts *C* by weight. The specific gravities of *A*, *B*, and *C* are 0.79, 0.98, and 1.16, respectively. Since no weighing equipment is available, the mixture must be made by adding measured volumes of the liquids. Calculate the volumes of *B* and *C* to add to a unit volume of *A* in order to have the correct composition.

1-23. A company has a contract to buy NaCl of 98% purity (2% insoluble impurity) for \$50/ton delivered. Its last shipment of 10 tons was only 90% pure (10% insoluble impurity).

a. How much should it pay for the shipment?

b. How much of this 90% material should be added to 2000 gal of water to make a 5%w NaCl solution (1 gal H_2O weighs 8.34 lb)?

1-24. Real gases, which do not obey the perfect-gas law, frequently follow the van der Waals equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

where p = absolute pressure
T = absolute temperature
V = molar volume
a, b, and R = constants

The units vary, according to the system used. For water vapor,

$$a = (20{,}600)\ \frac{(\text{lb/in.}^2)(\text{ft}^6)}{(\text{lb mole})^2}$$

$$b = 0.489\ \text{ft}^3/\text{lb mole}$$

and

$$R = (10.73)\ \frac{(\text{lb/in.}^2)(\text{ft}^3)}{(\text{lb mole})(^\circ\text{R})}$$

when the units of p are lb/in.^{2} and the units of T are °R. Calculate the molar volume V of water vapor in ft^3/lb mole when $p = 1500$ and $T = 1160$. Use both graphical and numerical methods.

1-25. Your company purchases a water solution containing three chemicals, *A*, *B*, and *C*. A recent shipment of 5 tons contains 6%w *A*, 13% *B*, and 19% *C*. The bill submitted by the supplier is for \$1125.00. This does not include shipping, which is a separate item. Your superior feels he is being overcharged and asks you to check. In looking over past records, you find this information:

Shipment	Tons shipped	% *A*	% *B*	% *C*	Total cost, \$
1	3	10	6	23	589.90
2	2	10	12	20	461.60
3	3	7	10	22	654.60

What is your report to your supervisor?

1-26. In a process you are investigating, one of the items of data taken is the rate of flow of steam to a heater. The following values are taken over a test period:

Time, hr.....	0	1	2	3	4	5	6
Rate, lb/hr.....	4000	4280	4440	4350	3920	3000	480

Because of the sudden drop in steam consumption, the process is stopped after 6 hr. Calculate the total amount of steam used and the mean value of the rate by

a. The trapezoid rule

b. Simpson's rule

c. Graphical integration

1-27. Demonstrate by a numerical example the validity of the iterative formula for cube root:

$$a_{n+1} = \left(\frac{1}{3}\right)\left(\frac{b}{a_n^2} + 2a_n\right)$$

where b = number whose cube root is to be found
a_n = previous trial cube root
a_{n+1} = next trial
For example, find the cube root of 27, using a_0, the first trial value, of 10.

Chapter 2

CHEMICAL AND PHYSICAL PRINCIPLES

An old man who sold ice at a summer resort approached one of his customers. "Ed," he said, "You're a college feller. I'd like you to help me with some figurin'. I buy ice for 50 cents a block and I sell it for 30 cents a block. I want to figure out how much profit I'm makin'."

"Profit!" Ed exclaimed. "You're losing money! If you buy a block for 50 cents and sell it for 30, you're losing 20 cents a block!"

"But," the old man protested, "I get four blocks from a block."

Ambiguity in scientific writing is usually much less obvious, and therefore much more serious, than it is in the above story. It can be avoided only by proper use of properly defined terms. Therefore we have taken the liberty of defining the terms which are of importance in this text even though many of them should be familiar to you from previous courses. Most of the familiar terms are defined in this chapter in which we review chemical and physical principles.

CHEMICAL FORMULAS

Chemical information is expressed by means of chemical formulas and chemical equations. The formulas and equations may be considered part of a code designed for cryptic presentation of information. The key to the code is the atomic weight table of the elements. The atomic weight table does not indicate the weights of the atoms. It indicates their relative weights, and, if it were properly named, it would be called the "relative atomic weight table." Oxygen has been chosen as the basic element and assigned an "atomic weight" of 16. The fact that the atomic weight of carbon is given as 12 means simply that one atom of carbon weighs twelve-sixteenths as much as one atom of oxygen.

In ordinary chemical reactions atoms are indivisible. Therefore the chemical compounds formed by ordinary chemical reactions are composed of molecules which contain whole numbers of atoms of various elements. A chemical formula indicates the number of atoms of each element in a molecule. With the aid of the atomic weight table it is

possible to calculate the percentage by weight of each element in a compound from the formula of that compound. Try the following problem, and then examine the two solutions:

Example 2-1. Carbon monoxide has the formula CO. The atomic weight of carbon is 12.0, and that of oxygen is 16.0. What is the weight per cent of carbon in CO?

Solution 1

Basis: Enough CO to contain 12 g of carbon. Since the formula shows that each atom of carbon is united with one atom of oxygen, an amount of CO that contains 12 g of carbon will contain 16 g of oxygen.

Therefore,
$$\left(\frac{12 \text{ g C}}{28 \text{ g CO}}\right)(100) = 42.8\%\text{w}$$

Solution 2

Basis: One molecule of CO. Let the weight of one atom of carbon be A g. One atom of oxygen weighs $(^{16}/_{12})(A \text{ g})$. One molecule of CO weighs $(^{28}/_{12})(A \text{ g})$. The weight per cent of carbon is

$$\left(\frac{A \text{ g C}}{(^{28}/_{12})(A \text{ g CO})}\right)(100) = 42.8\%\text{w}$$

Solutions 1 and 2 are both correct, but Solution 1 is preferable because it establishes a method of attack that is mathematically convenient. It simplifies the consideration of weight relationships by employing as a basis a weight in grams of carbon numerically equal to its atomic weight. Such a weight quantity is called a *gram atom* and is commonly defined, for any element, as "the atomic weight in grams." Since a gram atom of one element contains the same number of atoms as a gram atom of any other element, gram atoms are combined in a compound in the same simple whole-number proportions in which the atoms are combined in a molecule of that compound.

In Solution 1 it was explained that 12 g of carbon (1 gram atom) contains the same number of atoms as does 16 g of oxygen (1 gram atom). The chemical formula, CO, told us that one atom of carbon is combined with one atom of oxygen. With the aid of the gram-atom concept, the chemical formula now tells us that 1 gram atom of carbon is combined with 1 gram atom of oxygen, and therefore that 12 g of carbon is combined with each 16 g of oxygen, without even a momentary concern over the weight of one atom of either element.

This concept of the gram atom makes chemical writing and speech both simpler and clearer. They are simpler because simple whole numbers express the proportions between the gram atoms of various elements. They are clearer because the chemical formulas can immediately be

visualized, once the numbers of gram atoms are known. This is illustrated by the following statements:

1. In CH_4 12 g of carbon is combined with 4 g of hydrogen, and in CCl_4 12 g of carbon is combined with 142 g of chlorine.

2. In CH_4 1 gram atom of carbon is combined with 4 gram atoms of hydrogen, and in CCl_4 1 gram atom of carbon is combined with 4 gram atoms of chlorine.

CHEMICAL EQUATIONS

A chemical equation, as used in stoichiometry, has two main functions. The first function is a qualitative one. It is simply to tell what reacts and what is produced. The second function is a quantitative one. It is to express the composition of, and the quantitative relationships between, the materials involved. We have seen how the chemical formulas, which tell what reacts and what is produced, also indicate the composition of the various compounds. The gram-atom concept, which simplifies the calculation of the weights of elemental material in chemical compounds, has its analogue in the gram-molecule concept, which simplifies the calculation of the weights of chemical compounds involved in a chemical reaction. A gram molecule (called a *gram mole* or *gram mol*) is commonly defined, for any compound, as the "molecular weight in grams."

Since the molecular weight is calculated from the atomic weights, it also is a relative weight. The fact that the molecular weight of carbon monoxide is 28 means simply that a molecule of carbon monoxide weighs $^{28}/_{16}$ as much as an atom of oxygen. A gram mole of any compound contains the same number of molecules as a gram mole of any other compound. Note also that the number of molecules in a gram mole is the same as the number of atoms in a gram atom. A chemical equation, which expresses the relative proportions of the molecules in a chemical reaction, also expresses the relative proportions between the gram moles. The same simplification and clarification of chemical language follow from the use of the gram mole as was the case with the gram atom. The following equivalent statements illustrate this:

1. Forty grams of NaOH reacts with 36 g of HCl to produce 58 g of NaCl and 18 g of H_2O.

2. One g mole of NaOH reacts with 1 g mole of HCl to produce 1 g mole of NaCl and 1 g mole of H_2O.

Although gram atoms and gram moles have been used exclusively in the above illustrations, it should be realized that any unit of mass may be employed. For instance, a pound mole of oxygen is 32 lb, an ounce mole is 32 oz, a ton mole is 32 tons, etc. It is suggested that you adopt the convention (employed throughout the remainder of this book) of

writing grammole and poundmole (abbreviated gmole and lbmole) and tonmole in order to emphasize the fact that these quantities do not have the units of grams times "moles," or pounds times "moles," or tons times "moles" but have only the units of mass. They represent specific amounts of grams, pounds, or tons only when they are combined with a label indicating a chemical element or compound.

At this point it is evident that one equation, like one picture, is worth a thousand words. But before we carry the analogy too far, let us remember that an equation, unlike a picture, must tell the same story to different observers. This is possible only if the concepts which have so far been discussed are thoroughly understood by each observer. In addition, calculations which involve the equations must be expressed in such a way that they are readily understandable to others. To this end we shall define certain terms which you will find useful when doing calculations based on chemical equations.

The *limiting reactant* is the one which is present in least stoichiometric proportion.

An *excess reactant* is any reactant which is present in excess of an amount stoichiometrically equivalent to the quantity of the limiting reactant.

The excess (sometimes called the *theoretical excess* or *true excess*) amount of a reactant is the amount in excess of the quantity stoichiometrically equivalent to the quantity of the limiting reactant.

The *theoretically required* amount of a reactant is the amount stoichiometrically equivalent to the quantity of the limiting reactant.

The *per cent excess* of a reactant is the true excess expressed as a percentage of the theoretically required amount of that reactant. (Note that per cent excess is calculated from a knowledge of the chemical equation and amounts of reactants supplied only. The actual amount of products formed does not affect the calculation.)

The *degree of completion* of a reaction is the percentage of the limiting reactant which reacts.

The *percentage conversion* of any reactant is the percentage of the amount originally present which reacts.

The following example further illustrates these terms.

Example 2-2. Nitrogen and hydrogen react under certain conditions to form ammonia, according to the following equation:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The double arrow indicates that this is a reversible reaction. At some time after the reactants have been brought together, ammonia will be dissociating into nitrogen and hydrogen as fast as nitrogen and hydrogen are reacting to form ammonia. At this time no further change in con-

centration of any compound can occur, and the system is said to have reached "equilibrium."

Suppose that 280 lb of nitrogen and 64.5 lb of hydrogen are brought together and allowed to react at 515°C and 300 atm pressure, and from experimental measurements it is found that there are 38.0 lbmole of gases present at equilibrium.

a. How many poundmoles of nitrogen, hydrogen, and ammonia are present at equilibrium?

b. Which is the limiting reactant, and which is the excess reactant?

c. How much excess hydrogen is there?

d. What is the amount of theoretically required hydrogen, and what is the per cent excess hydrogen?

e. What is the degree of completion of the reaction?

f. What is the percentage conversion of hydrogen to ammonia?

Solution

Gases initially present:

$$(64.5 \text{ lb } H_2)\left(\frac{1 \text{ lbmole } H_2}{2.02 \text{ lb } H_2}\right) = 32.0 \text{ lbmole } H_2$$

$$(280 \text{ lb } N_2)\left(\frac{1 \text{ lbmole } N_2}{28.0 \text{ lb } N_2}\right) = 10.0 \text{ lbmole } N_2$$

Let x = lbmole N_2 used in the reaction.

Then	$3x$ = lbmole H_2 used
and	$2x$ = lbmole NH_3 formed
Therefore	$10 - x$ = N_2 left after reaction
and	$32 - 3x$ = H_2 left

At equilibrium the lbmole of $H_2 + N_2 + NH_3$ must equal 38.

Thus	$(32 - 3x) + (10 - x) + 2x = 38$
and	$x = 2$ lbmole
Therefore	the lbmole of $N_2 = 10 - x = 8$
	the lbmole of $H_2 = 32 - 3x = 26$
	the lbmole of $NH_3 = 2x = 4$

b. Which is the limiting reactant, and which is the excess reactant?

Solution. It takes only 30 lbmole of hydrogen to react with 10 lbmole of nitrogen. Therefore the hydrogen is present in excess, and the nitrogen is the limiting reactant.

c. How much excess hydrogen is there?

Solution. Thirty poundmoles of hydrogen is equivalent to 10 lbmole of nitrogen. Therefore the excess of hydrogen is 2 lbmole.

d. What is the theoretically required hydrogen, and what is the per cent excess hydrogen?

Solution. The theoretically required hydrogen is 30 lbmole. The per cent excess of hydrogen is $(\frac{2}{30})(100) = 6.67\%$.

e. What is the degree of completion of the reaction?

Solution. Since 2 lbmole of nitrogen reacts, the degree of completion is

$$(\frac{2}{10})(100) = 20\%$$

f. What is the percentage conversion of hydrogen to ammonia?

Solution. There is 32 lbmole of hydrogen originally present, and 6 lbmole react. Therefore $(\frac{6}{32})(100) = 18.75\%$.

When a compound reacts to give more than one product, the percentage total conversion (the percentage of the reactant which reacts to form all the products) should also be given.

The above definitions, together with the stoichiometric principles previously discussed, make it possible to recognize, interpret, and record the information conveyed by a chemical equation. It is very important to realize, however, that the ability of the equation to convey information is limited. The important limitations of a chemical equation are as follows:

1. It does not tell whether a reaction will proceed or not. It simply indicates the reacting proportions if it does proceed.
2. It does not indicate the rate of reaction.
3. It does not indicate the degree of completion of the reaction.
4. It does not indicate the best conditions for the reaction.

TEMPERATURE

Before we proceed with our discussion of physical-chemical principles, we must define and discuss the concepts of temperature and pressure.

The temperature scales commonly employed are the Fahrenheit, the centigrade, the Rankine, and the Kelvin. Figure 2-1 represents these scales.

The points designated as A and B are the freezing and boiling points of water, respectively. On the Fahrenheit scale, the freezing point is 32° and the boiling point is 212°. The corresponding values on the centigrade scale are 0° and 100°. Since there are 180 Fahrenheit degrees in the range covered by 100 centigrade degrees, we may conclude that $1\ \text{C}^\circ \approx 1.8\ \text{F}^\circ$.

Attempt the following problem, and then examine the various solutions:

Example 2-3

a. Convert a temperature of 20°C to the corresponding Fahrenheit temperature.

b. Convert a temperature of 68°F to the corresponding centigrade temperature.

Solution 1

a. The temperature of 20°C is 20 C° above the freezing point of water. (Note again the difference between °C and C°. 20°C is a temperature, but 20 C° is not. It is simply a number of degrees.) (20 C°)(1.8 F°/C°) = 36 F° above the freezing point of water. Therefore the Fahrenheit temperature is 36 + 32 = 68°F.

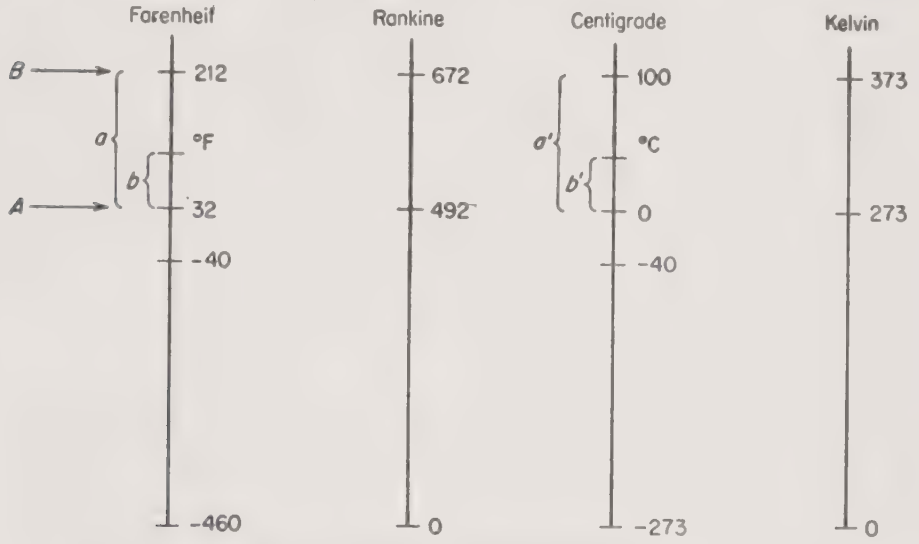


FIG. 2-1. Common temperature scales.

b. The temperature of 68°F is 36 F° above the freezing point of water. (36 F°)(1 C°/1.8 F°) = 20 C° above the freezing point. The centigrade temperature is 0 + 20 = 20°C. The above reasoning processes when written in equation form give

$$°C = (5/9)(°F - 32)$$

Solution 2

a. Let point F represent the unknown Fahrenheit temperature and point C represent the known centigrade temperature (20°C). Let a' represent the number of centigrade degrees between the freezing and boiling points of water and b' represent the number of centigrade degrees between the temperature under consideration (20°C) and the freezing point of water. Let a and b represent corresponding quantities for the Fahrenheit scale. Then,

$$\frac{b}{a} = \frac{b'}{a'}$$

Therefore,

$$\frac{F - 32}{212 - 32} = \frac{20 - 0}{100 - 0}$$

and

$$F = 68°F$$

b. Let point C represent the unknown centigrade temperature and

point F represent the known Fahrenheit temperature (68°F). The same reasoning as before leads to the statement that

$$\frac{68 - 32}{212 - 32} = \frac{C - 0}{100 - 0}$$

and

$$C = 20°C$$

Solution 3

a. This method is called the "rule of 40." It is based on the fact that −40°F = −40°C. The temperature, 20°C, is 60 C° above −40°C. It is also 60 C° above −40°F. Since 60 C° is equivalent to 108 F°, the temperature under consideration is 108 F° above −40°F. The temperature is therefore 68°F.

b. The temperature 68°F is 108 F° or 60 C° above −40°F. It is also 60 C° above −40°C. The temperature is therefore 20°C.

Note that the first step in either conversion is to add 40 and the last step is to subtract 40. You may quickly decide whether to multiply or divide by 1.8 in the middle step, since you know whether you want a larger or smaller numerical answer.

There are many logical ways to convert a particular temperature into the equivalent temperature on a different scale. The above problem and its several solutions show the type of reasoning involved. It does not matter which method you use, as long as you use it by thinking and not by memorizing a formula.

Absolute Temperature Scales. Early investigators found that the change in the pv (pressure times volume) product of a gas was directly proportional to the change in its temperature. Thus, a change of two degrees caused twice the change in the pv product that a change of one degree caused. It was determined experimentally that the pv product of a gas decreased by $\frac{1}{460}$ of its value at 0°F for each 1 F° decrease in temperature. Therefore the pv product would apparently become zero at −460°F. The investigators reasoned that this must be the lowest temperature that could be reached and called it *absolute* zero. A temperature scale on which this point was represented by zero was called an *absolute temperature scale.* The absolute temperature scale which employs the Fahrenheit degree as its basic unit is called the *Rankine scale;* that employing the centigrade degree is called the *Kelvin scale.*

Examination of Fig. 2-1 shows the relationships between the centigrade and Kelvin and between the Fahrenheit and Rankine scales. The relation between Rankine and Kelvin temperatures is the same as that between Fahrenheit and centigrade degrees. On each temperature scale, the temperature is the number of degrees above the zero point. Since 0°R ≈ 0°K, the conversion of one temperature to another is similar to the conversion of a number of Fahrenheit degrees into a number of centi-

grade degrees, or vice versa. Notice also that a ratio of two absolute temperatures (commonly employed in gas calculations, as indicated later) has the same numerical value, whether it is expressed as a ratio of Rankine or of Kelvin temperatures.

To illustrate the above numerically, assume that it is desired to convert 68°F to centigrade, using absolute temperatures.

$$68°F \approx 68 + 460°R \approx 528°R$$

This means that 68°F is 528 R° above absolute zero in °R. It is also 528 R° above 0°K. Then it is 528/1.8 = 293 K° above 0°K, or 293°K. This corresponds to 20°C. Note that 1 K° ≈ 1 C° ≈ 1.8 F° ≈ 1.8 R°.

The values 273 and 460 are approximate figures used by engineers. The actual values of the absolute zero are still not known exactly, but the best recent information places absolute zero at

$$273.165 \pm 0.015\ C° \text{ below } 0°C$$
$$459.679 \pm 0.027\ F° \text{ below } 0°F$$

PRESSURE

Pressure is defined as "force per unit area." It is customary to talk about "kinds" of pressure in order to distinguish between the pressures resulting from different forces. Several kinds of pressure are discussed below.

A gas exerts a pressure by virtue of the impact of its molecules against the walls of a confining vessel. The magnitude of the pressure depends upon the number of molecules and upon their average kinetic energy. It is therefore a function of the amount of gas present and of its temperature.

A liquid, if allowed to evaporate in a confined space, produces a vapor that permeates the space above the liquid and exerts a pressure. At the beginning of such a process the pressure in the vapor space increases as the amount of vapor increases. If there is sufficient liquid present, a point is eventually reached at which the pressure in the vapor space is exactly equal to the pressure exerted by the liquid at its own surface in its effort to evaporate. At this point a dynamic equilibrium exists in which vaporization and condensation take place at equal rates and the pressure in the vapor space remains constant. The pressure exerted at equilibrium is called the *vapor pressure* of the liquid. The magnitude of this pressure depends on the temperature for a given liquid but not on the amount of liquid present. Vapor pressure is a property of the liquid. It is exerted by the liquid in response to the temperature whether or not there is any vapor present. It is defined in terms of equilibrium simply

because it is best measured at equilibrium, where the pressure of the vapor and the vapor pressure of the liquid are equal.

Solids, like liquids, exert a vapor pressure. Evaporation of solids (called sublimation) is noticeable only for those with an appreciable vapor pressure.

A stationary solid object exerts a force on the surface upon which it rests. The magnitude of the force depends upon the mass of the object and upon the magnitude and direction of any unbalanced external forces acting on the object. For example, a 1-in. cube with a mass of 1 lb at rest at sea level exerts a 1-lb force on the supporting surface because of the pull of gravity and nearly 15 lb more force because of the pressure of the atmosphere (14.7 lb/in.^{2}) acting upon the top of the cube. The pressure of the atmosphere acting on the sides of the cube results in a force of 14.7 lb acting inward on each side but does not influence the force exerted downward. We may note that one characteristic of a rigid solid is that it transmits a force in the direction of the force.

A stationary fluid exerts a pressure on the surface which it contacts. The magnitude of the pressure depends upon the mass of the fluid, upon the magnitude of the external force, and upon the area of the fluid over which the external force is applied. Consider a thin-walled rigid container of negligible mass with a neck 1 in.^{2} in area, holding a fluid which extends up into the neck. Assume for the moment that the weight of the fluid is negligible and that it is nonvolatile. The fluid and the container transmit a force to the supporting surface exactly as outlined for the solid object considered previously. How does the fluid transmit the force to the container? Remember that a fluid can flow in response to unbalanced forces and therefore it is stationary only when the forces acting at one point in the fluid are equal in all directions. First consider the force due to the atmosphere. At the surface of the liquid the atmosphere is exerting 14.7 lb force on the square inch of liquid, and since the liquid would flow if forces were unbalanced at any point, the liquid is exerting 14.7 lb force upward toward the atmosphere. The pressure in the liquid must be 14.7 lb/in.^{2} in order for the upward force at the 1 in.^{2} of exposed surface to be 14.7 lb. At a point in a plane immediately below the surface the pressure must also be 14.7 lb/in.^{2} if the same balance of forces is to result. By an extension of this reasoning it may be seen that the fluid exerts a uniform pressure of 1 atm against the entire surface of the container. The force exerted against a particular square inch of container area is balanced by the force exerted against the square inch of opposite area. However, the square inch of container area below the neck of the vessel has no container surface above it, and the force exerted upon it is unbalanced. It is felt as a downward force of 14.7 lb by the surface supporting the vessel. Note that we have

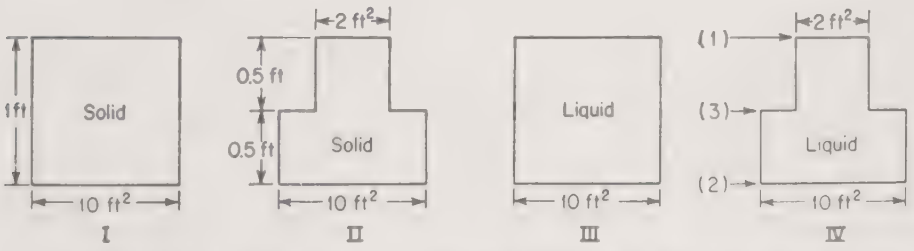
described the manner in which the force exerted by the atmosphere on the liquid surface is transmitted by the liquid. If the container widens below the neck, the force of the atmosphere on the outside surface is transmitted as described for a solid object.

Now suppose that the fluid has mass. In addition to the 14.7 lb/in.^{2} pressure on all surfaces of the container there will be pressure because of gravity. This pressure is determined only by the height of the fluid above a given point and the fluid density. This may be proved by considering any vertical column of fluid H ft high, with a horizontal cross-sectional area of A ft^2. The volume of the fluid is HA ft^3. If the fluid density is ρ lb/ft^3, the mass is $HA\rho$ lb. The fluid exerts a pressure of $(HA\rho/A)(g/g_c) = H\rho$ lb$_f$/ft^2. This pressure is independent of A and therefore is independent of the total mass of the fluid. It is zero at the surface of the fluid and increases directly as the depth of the fluid. The net unbalance of force acts downward and is equal to the force exerted by gravity on the entire fluid mass. Thus if the fluid has a mass of 2 lb the net force transmitted by the liquid in this case would be 16.7 lb.

In the case of a moving fluid, for example one flowing through a pipe, a pressure is exerted on the walls of the pipe exactly as described. This pressure, *exerted in all directions*, has to be measured at right angles to the direction of flow to avoid reading on the measuring device pressures caused by impingement of flowing fluid on it. The pressure with which we are concerned, exerted equally in all directions, is called *static pressure*. The pressure which is *created* by stopping the flow of fluid is called *velocity pressure*. We shall not be concerned with it in this text.

The following example applies the principles just discussed.

Example 2-4



Objects I and II are solid. The solid material of which they are composed is homogeneous and has a density of 64 lb/ft^3. Objects III and IV are containers filled with a liquid which has a density of 64 lb/ft^3. Plane 2 refers to the *inside* surface of the container in III and IV. In cases *a* to *d* below, the liquid has negligible vapor pressure.

a. What is the pressure at point 2 when the objects are in a vacuum, assuming that no vaporization of the liquid occurs?

Object I: $$\frac{640 \text{ lb}}{10 \text{ ft}^2} = \frac{64 \text{ lb}}{\text{ft}^2}$$

Object II: $$\frac{384 \text{ lb}}{10 \text{ ft}^2} = \frac{38.4 \text{ lb}}{\text{ft}^2}$$

Object III: $$(1 \text{ ft})\left(\frac{64 \text{ lb}}{\text{ft}^3}\right) = \frac{64 \text{ lb}}{\text{ft}^2}$$

Object IV: Same as III

Note that container III (not the liquid within the container) would exert 64 lb/ft² pressure against the supporting surface underneath it, whereas container IV would exert 38.4 lb/ft² pressure against its supporting surface (if negligible mass is assumed for the containers themselves and only the mass of the liquid in them is considered).

b. If a solid cylinder 2 ft² in area and weighing 20 lb were placed on the top of II, what would be the increase in pressure at planes 1 and 2?

At 1: $$\frac{20 \text{ lb}}{2 \text{ ft}^2} = \frac{10 \text{ lb}}{\text{ft}^2}$$ an increase of $\frac{10 \text{ lb}}{\text{ft}^2}$

At 2: $$\frac{404 \text{ lb}}{10 \text{ ft}^2} = \frac{40.4 \text{ lb}}{\text{ft}^2}$$ an increase of $40.4 - 38.4 = \frac{2 \text{ lb}}{\text{ft}^2}$

This is also equal to

$$\frac{20 \text{ lb}}{10 \text{ ft}^2} = \frac{2 \text{ lb}}{\text{ft}^2}$$

Note that the extra force of 20 lb was transmitted to area 2 but that the extra pressure of 10 lb/ft² was not. The increase in pressure at area 2 would be the same as the increase in pressure at 1 only if the areas were equal.

c. If a solid cylinder 2 ft² in area and weighing 20 lb were placed at the top of IV, inside the neck of the vessel so that the liquid supported the weight but could not escape around the weight, what would be the increase in pressure at planes 1 and 2?

At 1: $$\frac{20 \text{ lb}}{2 \text{ ft}^2} = \frac{10 \text{ lb}}{\text{ft}^2}$$ an increase of $\frac{10 \text{ lb}}{\text{ft}^2}$

At 2: $$\frac{10 \text{ lb}}{\text{ft}^2} + (1 \text{ ft})\left(\frac{64 \text{ lb}}{\text{ft}^2}\right) = \frac{74 \text{ lb}}{\text{ft}^2}$$ an increase of $\frac{10 \text{ lb}}{\text{ft}^2}$

Note that the pressure increase at plane 1 in the fluid is transmitted throughout the fluid.

d. If II is placed in the atmosphere at sea level, what are the pressures at planes 1 and 2?

At 1: $$\left(\frac{14.7 \text{ lb}}{\text{in.}^2}\right)\left(\frac{144 \text{ in.}^2}{\text{ft}^2}\right) = \frac{2117 \text{ lb}}{\text{ft}^2}$$

At 2: $$\frac{2117 \text{ lb}}{\text{ft}^2} + \frac{38.4 \text{ lb}}{\text{ft}^2} = \frac{2155.4 \text{ lb}}{\text{ft}^2}$$

The solution to *d* for plane 2 is different from the solution to *b* for plane 2 because the added pressure is not confined to area 1. The atmosphere acts also on area 3.

e. If IV is in the atmosphere at sea level and the liquid vapor pressure is 5 lb/ft², what are the pressures at 1 and 2?

At 1: $$\frac{14.7 \text{ lb}}{\text{in.}^2} \quad \text{or} \quad \frac{2117 \text{ lb}}{\text{ft}^2}$$

The vapor pressure is not added, because the atmosphere acts as a pressure regulator. Liquid vaporizes because of its vapor pressure, but it simply displaces some air, and the total pressure exerted at 1 remains 14.7 lb/in.².

At 2: $$\frac{2117 \text{ lb}}{\text{ft}^2} + \frac{64 \text{ lb}}{\text{ft}^2} = \frac{2181 \text{ lb}}{\text{ft}^2}$$

Fluid Heads. The magnitude of a particular pressure is often determined by measurement of the height of a column of liquid of known density which the pressure will support. If the liquid column employed has a vacuum at one end, as is the case with the mercury barometer, the pressure measured is an absolute pressure. For accurate work the temperature of the mercury is measured so that its exact density may be used in the pressure computations, and a correction is made for the vapor pressure of the mercury which is exerted in the evacuated space. For ordinary engineering calculations the vapor pressure of the mercury is negligible, and the mercury temperature (if not specified) is taken as room temperature (20°C ≈ 68°F).

Another common type of measuring device, the manometer, uses a liquid column with one end open to the atmosphere. The pressure computed from the liquid height and density may be added (algebraically) to the prevailing atmospheric pressure to compute the absolute pressure, or it may simply be stated as a *gauge* pressure (amount above atmospheric) or *vacuum* (amount below atmospheric).

Here again the temperature of the liquid is taken as room temperature if not specified. The vapor pressure need not even be considered because it has no effect, as shown in Example 2-4, part *e*.

It is common engineering practice to report a pressure as the height of a column of a liquid of known density. Such a height is called a *head* when it represents the amount by which the pressure exceeds atmospheric. It is called a *draft* when it represents the amount by which the

specified pressure is less than atmospheric. These expressions are not usually employed when the measuring liquid is mercury.

Figure 2-2 indicates the relationships between "absolute pressure," "gauge pressure," "vacuum," "head," and "draft."

It is convenient to know the standard atmospheric pressure in various

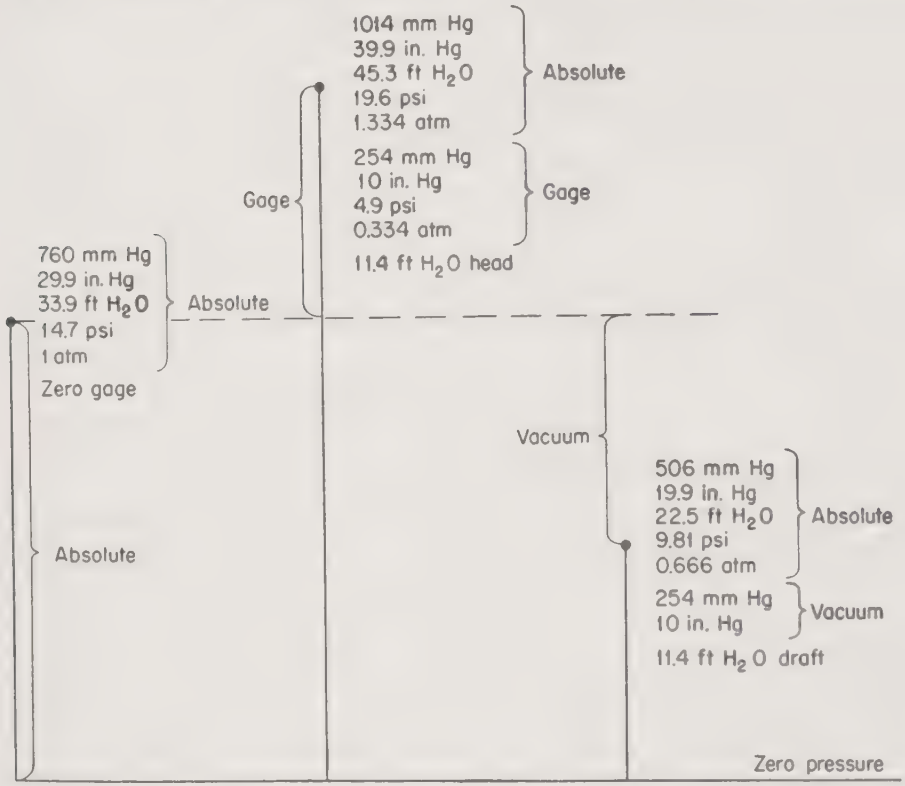


Fig. 2-2. Methods of expressing pressure.

units, for aid in conversion calculations. Sea-level pressure is 14.7 lb/in.^{2}, or 33.9 ft of water, or 29.9 in. Hg, or 760 mm Hg. With this information in mind, make the following conversions:

Example 2-5

a. Convert a pressure of 10 lb/in.^{2} into mm Hg.

$$\left(\frac{10 \text{ lb}}{\text{in.}^2}\right)\left(\frac{760 \text{ mm Hg}}{14.7 \text{ lb/in.}^2}\right) = 517 \text{ mm Hg}$$

Without the aid of the standard-pressure equivalents, the calculation would be

$$\left(\frac{10 \text{ lb}}{\text{in.}^2}\right)\left(\frac{144 \text{ in.}^2}{\text{ft}^2}\right)\left(\frac{1 \text{ ft}^3 \text{ Hg}}{(13.6)(62.4) \text{ lb Hg}}\right)\left(\frac{30.5 \text{ mm Hg}}{\text{ft Hg}}\right) = 517 \text{ mm Hg}$$

b. Convert a pressure of 517 mm Hg into feet of water.

$$(517 \text{ mm Hg}) \left(\frac{33.9 \text{ ft } H_2O}{760 \text{ mm Hg}}\right) = 23.0 \text{ ft } H_2O$$

Without the aid of the standard-pressure equivalents, the calculations would be

$$(517 \text{ mm Hg}) \left(\frac{1 \text{ ft Hg}}{30.5 \text{ mm Hg}}\right) \left(\frac{(13.6)(62.4) \text{ lb}}{\text{ft}^3 \text{ Hg}}\right) \left(\frac{\text{ft}^3 H_2O}{62.4 \text{ lb}}\right) = 23.0 \text{ ft } H_2O$$

One could also use the ratios of the specific gravities. Thus,

$$(517 \text{ mm Hg}) \left(\frac{1 \text{ ft Hg}}{30.5 \text{ mm Hg}}\right) \left(\frac{13.6 \text{ ft } H_2O}{1 \text{ ft Hg}}\right) = 23.0 \text{ ft } H_2O$$

THE PERFECT-GAS LAWS

In an industrial process or operation, a record must be kept of the quantities of materials used and produced. It is more convenient to measure the volumes of liquids or gases than it is to measure their weights. But the basic quantities necessary for calculation are weight quantities, and since the weight of a certain volume depends upon its pressure and temperature, pressure and temperature records are also kept.

In order to convert pressure-volume-temperature information into weight, the calculator must know some correlating relationship. If all substances in all states (gaseous, liquid, or solid) exhibited the same variations of volume with changing pressure and temperature, a universal law could be expounded, expressing the relationships between the variables and permitting the calculation of weight from PVT information only. Since substances are composed of atoms or molecules, this universal law would really express the habits of these particles in occupying space and exerting pressure and would be written in terms of moles so that equal numbers of particles would be considered.

However, the volume occupied and pressure exerted by a given number of atoms or molecules at a given temperature are affected by their physical nature. For example, the volume occupied by the particles themselves (as distinct from total volume, which includes the space between them) is different for different substances. Also, the atoms or molecules of an element or compound exert certain forces upon each other, such as gravitational forces, which are proportional to mass, and magnetic forces, which depend upon electrical configuration. These forces help to determine the volume of a given number of molecules and the pressure which those molecules exert, at a given temperature.

In the liquid and solid states, where the particles are relatively close together, there is no general correlation between number of molecules, volume, pressure, and temperature. A general correlation, or universal

law, is possible only for the gaseous state, and even then only when the average distance between the particles is sufficiently great that the intermolecular forces are negligible and the volume of the molecules themselves is negligible compared with the total volume. It is postulated that an ideal gas would be one for which this was always true, and the law is called the ideal-, or perfect-, gas law.

Early investigators discovered the correlating relationships by working with the so-called "noncondensable" gases at moderate pressures and temperatures. Robert Boyle, in 1660, reported that the volume of a gas varied inversely as the absolute pressure, at constant temperature. Both Charles and Gay-Lussac announced in 1802 that the volume varied directly as the absolute temperature at constant pressure.

Gay-Lussac expressed the proportionality of reacting gas volumes but could not explain such a reaction as the formation of nitric oxide. His concept of the reaction was

$$2N + 2O \rightarrow 2NO$$

and he was confused by the fact that no volume change occurred. Amadeo Avogadro in 1811 drew a distinction between "molecules integrantes" (still called "molecules") and "molecules elementaires" (now called "atoms"). He proposed his famous hypothesis that "equal volumes of different gases under the same conditions of temperature and pressure contain an equal number of molecules." This means that a mole of gas, at a certain pressure and temperature, occupies the same volume as a mole of any other gas at the same pressure and temperature. Avagadro stated correctly that the equation for the formation of nitric oxide was

$$N_2 + O_2 \rightarrow 2NO$$

All these conclusions were drawn from experiments during which the gaseous materials were exhibiting ideal behavior, within the experimental accuracy of the measuring devices used.

These observations form the basis of the perfect-gas law. They may be combined into the equation

$$PV = NRT \tag{2-1}$$

where P = absolute pressure
V = volume of gas
N = number of moles present
T = absolute temperature
R = a constant, the numerical value of which depends upon the units used

Gas Constant or Equivalent Quantity. The gas constant R, called the "perfect- or ideal-gas constant," is a natural constant. Its value

may not be derived by abstract mathematical reasoning. It can be established only by careful experimental measurement of the physical behavior of gases. It is necessary to memorize the value of the gas constant, or equivalent information, in order to solve gas problems. The equivalent information is the volume of one mole at a given temperature and pressure. The following example illustrates the two methods of approach:

Example 2-6

a. The value of the ideal-gas constant is 0.729 (atm)(ft³)/(lbmole)(°R). How many poundmoles of nitrogen will occupy 1000 ft³ at a pressure of 16 lb/in.² and a temperature of 400°K?

Solution

$$PV = NRT$$

$$\left(\frac{16 \text{ lb}}{\text{in.}^2}\right)\left(\frac{1 \text{ atm}}{14.7 \text{ lb/in.}^2}\right)(1000 \text{ ft}^3) = (N)\left(\frac{0.729(\text{atm})(\text{ft}^3)}{(\text{lbmole})(°\text{R})}\right)(400)(1.8)(°\text{R})$$

$$N = 2.07 \text{ lbmole}$$

b. Defining standard conditions (SC) as the freezing temperature of water and one atmosphere pressure and solving the perfect-gas law for the volume of 1 mole of gas, we find that 1 gmole occupies 22.4 liters and 1 lbmole occupies 359 ft³. These quantities are often referred to as molar volumes at standard conditions. Therefore, if the volume of a gas is found at standard conditions, this volume may be divided by the molar volume to determine the number of moles. Answer the question of part *a* on the basis of this knowledge.

$$\left[(1000 \text{ ft}^3)\left(\frac{273°\text{K}}{400°\text{K}}\right)\left(\frac{16 \text{ lb/in.}^2}{14.7 \text{ lb/in.}^2}\right)\right]^* \left(\frac{1 \text{ lbmole}}{359 \text{ ft}^3}\right) = 2.07 \text{ lbmole}$$

Comparison of *a* and *b* reveals that calculation *a* has (1.8)(0.729) where *b* has 359/273. That this latter is the equivalent of the constant may be seen from the following:

$$PV = (NRT) \qquad (1 \text{ atm})(359 \text{ ft}^3) = (1 \text{ lbmole})(R)(273°\text{K})$$

The second method of solution is employed in this text. It is preferred simply because it is similar in form to the most common type of gas calculation. This calculation involves the determination of the final volume of a given quantity of gas, if the initial volume, pressure, and temperature and the final pressure and temperature are known.

If the conditions of temperature and pressure on a given quantity of

* These brackets have a special significance. They indicate that the quantities contained therein are at standard conditions. This is merely a calculation habit of the authors. It is employed here because it has been found useful by many students.

gas are changed and the number of moles does not change, the gas law yields this expression relating the initial and final conditions:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{2-2}$$

The subscripts 1 and 2 refer to initial and final condition, respectively. This equation is useful for determining the change in volume which will occur when the temperature and pressure are changed and is also the basis of a convenient method for determining the number of moles in a given quantity of gas, as shown in Example 2-6 part *b*.

In keeping with our basic tenet of reasoning rather than memorizing, we proceed as shown below.

Example 2-7. A gas occupies 1000 ft³ at 400°K and 16 psia. What volume would it occupy at 273°K and 14.7 psia?

Solution. The original volume will change in response to the temperature change and also in response to the pressure change. The temperature decreases and tends to decrease the volume. The pressure decreases and tends to increase the volume. If we multiply the volume first by the temperature ratio and then by the pressure ratio, in such a way as to express these tendencies, we can calculate the final volume.

$$\left[(1000 \text{ ft}^3)\left(\frac{273}{400}\right)\left(\frac{16}{14.7}\right)\right] = 742 \text{ ft}^3 \qquad \text{at SC}$$

This is, of course, the same result that would be obtained from Eq. (2-2). In an analogous manner, it is possible to calculate the final pressure or temperature if either of these is the unknown quantity.

In Example 2-6, part *b*, the only reason for converting the gas volume to standard conditions was that the factor 359 ft³/lbmole, which was to be used, was also at standard conditions. The volume per poundmole at any arbitrarily chosen temperature and pressure would do equally well, but it is customary to use the volume at standard conditions. You should realize that you are merely finding the volume which would be occupied if the gas obeyed the perfect-gas law at standard conditions. It should really be called the equivalent volume at 1 atm pressure and 0°C. It is not necessary that the real gas under consideration be an ideal gas at standard conditions, because it is reduced to them only on paper and not in actuality. It must, however, be a perfect gas at the pressure and temperature at which its volume is measured.

Gaseous Mixtures. Let us consider a mixture of gases under conditions such that each individual gas behaves ideally. Each gas occupies the full volume, in spite of the presence of the other gases. The pressure which it exerts in the full volume, at the temperature of the mixture, depends upon the number of moles of the particular gas. It does not

depend upon the nature of the gas or upon the nature of the other gases in the mixture, since these are ideal gases and intermolecular forces are negligible. The total pressure of the mixture is the sum of the individual pressures. Dalton, in 1805, stated that the total pressure exerted by a mixture of gases is the sum of the pressures which the individual gases exert, when present alone in the full volume at the temperature of the mixture. This is strictly true only for a mixture of ideal gases. The term *partial pressure* is used both for the pressure exerted by one gas in a gas mixture and for the pressure which it would exert alone in the full volume. These quantities are identical only for ideal gases.

Remember that the basic purpose of PVT measurements in stoichiometry is to enable us to calculate the moles (or weight) of the gaseous substances. We may readily calculate the total number of moles in a mixture of ideal gases from the total pressure, total volume, and temperature of the mixture, because each gas in the mixture obeys the ideal-gas law and therefore the total mixture must also obey it. Mathematically, if

N = total moles

$n_A, n_B, \ldots$ = moles of components $A, B, \ldots$

P = total pressure

$p_A, p_B, \ldots$ = partial pressures of $A, B, \ldots$

then

$$p_A V = n_A RT$$
$$p_B V = n_B RT \qquad (2\text{-}3)$$

Adding the equations for all the components,

$$V\Sigma p = RT\Sigma n$$

Since Σp = total pressure = P

and Σn = total moles = N

the above equation reduces to

$$PV = NRT$$

Thus the perfect-gas law may be applied to the mixture of perfect gases.

We may calculate the moles of any individual gas from the total volume and temperature of the mixture and partial pressure of the individual gas. Therefore we could satisfactorily describe a mixture of gases by giving the total volume, the temperature, and the partial pressures of the components. With this information it would be possible to calculate the total moles of mixture, moles of each component, total weight, weight of each component, and the mole and weight fractions and percentages of each component. Since the relative number of moles of each component determines its relative pressure, pressure fraction is equal to mole fraction. This may be seen mathematically if we express the moles in terms of the pressure and write the expression for the mole fraction.

Since $$n_A = \frac{p_A V}{RT}$$

and $$N = \frac{PV}{RT}$$

then $$\frac{n_A}{N} = \frac{p_A}{P} = y_A \tag{2-4}$$

Note also that mole ratio, n_A/n_B, equals pressure ratio, p_A/p_B.

As explained in the following section (Condensable Gases), the partial pressures of condensable gases may be determined experimentally without difficulty. However, the partial pressure of a noncondensable gas can rarely be determined by direct measurement. The composition of a mixture of noncondensable gases is determined by measuring the *partial volume* of each gas.

The partial volume is defined as the volume which the gas would occupy if it alone were present at the temperature and full pressure of the mixture. Amagat observed that the total volume occupied by a mixture of gases is the sum of the volumes which the individual gases occupy when present alone at the temperature and pressure of the mixture. This is strictly true only for a mixture of ideal gases. The term "partial volume" is used both for the volume defined above and for the increase in volume of a mixture of gases which results from the addition of another gas. These quantities are identical only for ideal gases. If

V = total volume

and $v_A, v_B, \ldots$ = partial volumes of components $A, B, \ldots$

then $$Pv_A = n_A RT$$

and $$Pv_B = n_B RT \tag{2-5}$$

Adding the above equations for all the components,

$$P\Sigma v = RT\Sigma n$$

or $$PV = NRT$$

Dividing one of the equations for a pure component by the equation for the mixture,

$$\frac{v_A}{V} = \frac{n_A}{N} = y_A \tag{2-6}$$

This equation shows that the partial volume of any component of the mixture is equal to the mole fraction times the total volume. We may summarize the discussion on partial pressure and partial volume, for a perfect gas, by writing

$$\frac{p_A}{P} = \frac{v_A}{V} = \frac{n_A}{N} = y_A \tag{2-7}$$

or *pressure fraction equals volume fraction equals mole fraction.*

Occasionally it is desirable to work with weight fraction of gases in a mixture. This is not ordinarily done because no simple relationships exist between mole fraction, pressure fraction, and weight fraction.

The total weight (actually, mass) of a mixture of gases consisting of n_A mole of A, n_B mole of B, etc., where

$$M_A, M_B, \ldots = \text{molecular weights of } A, B, \ldots$$

is

$$W = n_A M_A + n_B M_B + \cdots = \Sigma nM \tag{2-8}$$

Then the weight fraction of a component is given by

$$\frac{n_A M_A}{\Sigma nM} = \frac{w_A}{W} = z_A \tag{2-9}$$

The average molecular weight of a mixture of gases is given by

$$M_{av} = \frac{\Sigma nM}{\Sigma n} = \frac{\Sigma nM}{N} \tag{2-10}$$

Then the weight fraction and mole fraction are related by the expression

$$z_A = \frac{n_A M_A}{N M_{av}} = \left(\frac{M_A}{M_{av}}\right)(y_A) \tag{2-11}$$

Thus any of the equations involving pressure and volume fractions may be written in terms of weight fraction as well as mole fraction, but the resulting equations are not as convenient to use as those involving mole fractions. These relationships are illustrated in the following problem:

Example 2-8. In 1000 ft³ of a mixture of H_2, N_2, and CO_2 at 250°F, the partial pressures of the three gases are 0.26 atm, 0.32 atm, and 1.31 atm, in the order named. Assuming that the gases behave ideally, answer the following:

a. How many poundmoles of hydrogen are there?
b. What are the mole fraction and mole percentage of hydrogen?
c. What is the pressure fraction of hydrogen?
d. What is the partial volume of hydrogen?
e. What are the volume fraction and volume percentage of hydrogen?
f. What is the weight of hydrogen?
g. What is the average molecular weight of the mixture?
h. What is the weight fraction of hydrogen?

Solution

a. Number of poundmoles of hydrogen

$$\left[(1000 \text{ ft}^3 \text{ H}_2)\left(\frac{0.26}{1}\right)\left(\frac{492}{710}\right)\right]\left(\frac{\text{lbmole}}{359 \text{ ft}^3}\right) = 0.501 \text{ lbmole H}_2$$

b. Mole fraction and percentage of hydrogen

$$\left[(1000 \text{ ft}^3 \text{ mixture})\left(\frac{0.26 + 0.32 + 1.31}{1}\right)\left(\frac{492}{710}\right)\right]\left(\frac{\text{lbmole}}{359 \text{ ft}^3}\right) = 3.65 \text{ lbmole mixture}$$

$$\frac{0.501 \text{ lbmole } H_2}{3.65 \text{ lbmole mixture}} = 0.138 \text{ mole fraction, or } 13.8\%\text{m}$$

The total moles of mixture could have been calculated from the knowledge that pressure fraction equals mole fraction, as follows:

$$(0.501 \text{ lbmole } H_2)\left(\frac{1.89 \text{ lbmole mixture}}{0.26 \text{ lbmole } H_2}\right) = 3.65 \text{ lbmole mixture}$$

c. Pressure fraction of hydrogen

$$\frac{0.26 \text{ atm}}{1.89 \text{ atm}} = 0.138 = \text{pressure fraction}$$

d. Partial volume of hydrogen. Partial volume is the volume at 1.89 atm and 250°F. Start with 1000 ft³ of H_2 at 0.26 atm and 250°F, and find the volume at 1.89 atm and 250°F.

$$(1000 \text{ ft}^3 H_2)\left(\frac{0.26}{1.89}\right) = 138 \text{ ft}^3$$

e. Volume fraction and percentage of hydrogen

$$\frac{138 \text{ ft}^3}{1000 \text{ ft}^3} = 0.138 = \text{volume fraction, or } 13.8\%\text{v}$$

f. Weight of hydrogen

$$(0.501 \text{ lbmole } H_2)\left(\frac{2.02 \text{ lb } H_2}{\text{lbmole } H_2}\right) = 1.10 \text{ lb } H_2$$

g. Average molecular weight of the mixture
Basis: 100 lbmole of mixture

Component	Mole = n	M	$w = nM$
H_2.....	$(100)\left(\frac{0.26}{1.89}\right) = 13.8$	2.02	27.8
N_2.....	$(100)\left(\frac{0.32}{1.89}\right) = 16.9$	28.0	474
CO_2.....	$(100)\left(\frac{1.31}{1.89}\right) = 69.3$	44.0	3060
			3561.8

$$\frac{3562 \text{ lb}}{100 \text{ lbmole}} = \frac{35.6 \text{ lb}}{\text{lbmole}} = \text{average molecular weight} = M_{av}$$

h. Weight fraction of hydrogen

$$\frac{27.8}{3562} = 0.0078 = \text{weight fraction of } H_2$$

or

$$\left(\frac{0.138 \text{ lbmole } H_2}{\text{lbmole mixture}}\right)\left(\frac{2.02 \text{ lb } H_2}{\text{lbmole } H_2}\right)\left(\frac{\text{lbmole mixture}}{35.6 \text{ lb mixture}}\right) = \frac{0.0078 \text{ lb } H_2}{\text{lb mixture}}$$

Some important conclusions concerning mixtures of ideal gases may be drawn from the above example. One is that mole fraction, volume fraction, and pressure fraction are equal. Another is that weight fraction is less desirable than either of the other fractions for calculation purposes, just as weight was less desirable than moles in dealing with chemical equations. Take special note in the example that the partial pressure of each gas is proportional to the number of moles of it present. This means that the partial pressure can be calculated if the mole fraction and total pressure are known. If y_A = mole fraction of gas A, then $p_A = y_A P$. This was shown in Eq. (2-4). This statement is true only when each gas is ideal. It is commonly said to apply "when Dalton's law is obeyed."

Condensable Gases (Vapors). One type of problem which requires the use of the partial-volume and partial-pressure concepts is encountered when one is dealing with gas mixtures containing condensable vapors. Even if all the gases present follow the perfect-gas law, the simplified equations such as (2-2) may not always be used, because of a change in the number of moles as a result of condensation or vaporization. For the purposes of this text, it may be assumed that the law is obeyed by each gaseous material unless and until it, itself, begins to condense.

As an example, consider the isothermal compression of a mixture of air and water vapor in which the partial pressure of the water vapor is originally one-half the vapor pressure of water at that temperature. When the total pressure is doubled, the partial pressures of all the gases are doubled, including that of the water, and the volume of the mixture is halved. At this point the partial pressure of the water equals its vapor pressure. If the compression is carried further, the partial pressure of all the other gases will increase, but, because of the condensation of the water vapor, its partial pressure will remain constant. The mole fraction of the water will decrease, and the total moles of gas will also decrease.

A discussion of the characteristics of gaseous mixtures containing a vapor is given in connection with the solution to the following problem:

Example 2-9

a. Five liters of a mixture of air and water vapor exists at 40°C and 762 mm Hg pressure. The partial pressure of the water vapor is 27.7 mm Hg.

b. The original mixture is heated at constant pressure to 60°C.

c. The original mixture is cooled at constant pressure to 20°C.

d. The original mixture is heated at constant volume to 60°C.

e. The original mixture is cooled at constant volume to 20°C.

f. The original mixture is expanded at constant temperature to 10 liters.

g. The original mixture is compressed at constant temperature to 1 liter.

MW $H_2O = 18$ MW dry air = 29.0
Vapor pressure of water at 20°C = 17.5 mm Hg
Vapor pressure of water at 40°C = 55.3 mm Hg
Vapor pressure of water at 60°C = 149 mm Hg
1 gmole of gas occupies 22.4 liters at SC

For each of the above conditions, what are the values of the following:

1. The partial pressure of water vapor
2. The partial pressure of dry air
3. The total pressure
4. The total volume
5. The grammoles of water vapor in the final mixture
6. The grammoles of dry air in the final mixture
7. The grammoles of water condensed

Solution

a. Conditions of the original mixture:

1. $p_{H_2O} = 27.7$ mm Hg (given)
2. $p_{air} = 762 - 27.7 = 734.3$ mm Hg
3. $P = 762$ mm Hg (given)
4. $V = 5$ liters (given)
5. $\left[(5 \text{ liters})\left(\frac{273}{313}\right)\left(\frac{762}{760}\right)\right]\left(\frac{\text{gmole}}{22.4 \text{ liters}}\right) = 0.1952$ gmole of mixture

$$(0.195)\left(\frac{27.7 \text{ gmole water vapor}}{762 \text{ gmole mixture}}\right) = 0.0071 \text{ gmole water vapor}$$

6. $0.195 - 0.0071 = 0.188$ gmole dry air

The grammoles of each material can also be calculated from the volume, temperature, and partial pressure of that material. For example,

$$\left[(5 \text{ liters})\left(\frac{273}{313}\right)\left(\frac{27.7}{760}\right)\right]\left(\frac{1}{22.4}\right) = 0.0071 \text{ gmole of water vapor}$$

It is possible to state the quantity of water vapor in three ways:
(1) There is 0.0071 gmole of water vapor.
(2) There is 5 liters of water vapor at 27.7 mm Hg and 40°C.

(3) There is (5)(27.7/762), or 0.164, liter of water vapor at 762 mm Hg and 40°C.

7. No water vapor condenses (given).

b. Conditions when the original mixture is heated at constant pressure to 60°C:

1. p_{H_2O} = 27.7 mm Hg (no change)
2. p_{air} = 734.3 mm Hg (no change)
3. P = 762 mm Hg (no change)
4. V = (5 liters)(333°K/313°K) = 5.32 liters
5. 0.0071 (no change) gmole water vapor
6. 0.188 (no change) gmole dry air
7. No water condenses.

If the original mixture is heated at constant pressure, no condensation can occur. Therefore the total moles and mole fraction of each component are unchanged. Since the total pressure is constant, if the mole fractions are constant, the partial pressures are also constant. Another way to state this is to say that all the gaseous materials obey the same gas law, and if the total pressure on the mixture is constant, the pressure of each gaseous material must be constant.

c. Conditions when the original mixture is cooled at constant pressure to 20°C:

1. If the original mixture is cooled at constant pressure, condensation may occur. If water condenses, the final volume cannot be calculated by applying the gas law to the total mixture, because it does not apply. The final partial pressure of the dry air cannot be calculated because the final volume is unknown. It is easy to decide whether condensation will occur or not. The final pressure of the water vapor would be 27.7 mm Hg if condensation did not occur. But at 20°C, the vapor pressure of water is 17.5 mm Hg. Therefore condensation does occur, and the final partial pressure of water vapor is 17.5 mm Hg.

2. p_{air} = 762 − 17.5 = 744.5 mm Hg .

3. P = 762 mm Hg (no change)

4. A convenient way to compute the final volume is to calculate the final volume of the dry air at its partial pressure since the air at its partial pressure occupies the full volume of the mixture.

$$(5 \text{ liters dry air})\left(\frac{293}{313}\right)\left(\frac{734}{744}\right) = 4.62 \text{ liters of total mixture}$$

5. There is 4.09 liters of water vapor at 20°C and 17.5 mm Hg.

$$\left[(4.62 \text{ liters})\left(\frac{273}{293}\right)\left(\frac{17.5}{760}\right)\right]\left(\frac{1}{22.4}\right) = 0.00442 \text{ gmole water vapor}$$

6. The air is not condensable. Therefore there is 0.188 gmole of dry air.

7. 0.00710 − 0.00442 = 0.00268 gmole water condenses.

d. Conditions when the original mixture is heated at constant volume to 60°C:

1. If the original mixture is heated at constant volume, no condensation occurs. Therefore the gas laws may be applied to the total mixture. Thus

$$p_{H_2O} = (27.7 \text{ mm Hg})(333/313) = 29.4 \text{ mm Hg}$$

2. $p_{air} = (734 \text{ mm Hg})(333/313) = 780 \text{ mm Hg}$
3. $P = 780 + 29.4 = 809.4 \text{ mm Hg}$
4. $V = 5$ liters (given)
5. 0.0071 gmole of water vapor (no change)
6. 0.188 gmole dry air (no change)
7. No water condenses.

e. Conditions when the original mixture is cooled at constant volume to 20°C:

1. If the original mixture is cooled at constant volume, condensation may occur. In order to determine whether it does or not, the partial pressure of the water vapor is calculated, assuming no condensation.

$$(27.7 \text{ mm Hg})(^{293}\!/_{313}) = 25.9 \text{ mm Hg}$$

But the vapor pressure of water at 20°C is only 17.5 mm Hg. Therefore condensation does occur, and the final partial pressure of water vapor is 17.5 mm Hg.

2. The dry air will obey the gas laws. Since its final volume is known,

$$p_{air} = (734 \text{ mm Hg})(^{293}\!/_{313}) = 690 \text{ mm Hg}$$

3. $P = 690 + 17.5 = 707.5 \text{ mm Hg}$
4. $V = 5$ liters (given)
5. $\left[\dfrac{(5 \text{ liters})(17.5)(273)}{(760)(293)}\right]\left(\dfrac{1}{22.4}\right) = 0.00479$ gmole of water vapor
6. 0.188 gmole (no condensation)
7. $0.0071 - 0.00479 = 0.00231$ gmole water condenses.

f. Conditions when the original mixture is expanded at constant temperature to 10 liters:

1. If the original mixture is expanded, no condensation will occur.

$$p_{H_2O} = (27.7 \text{ mm Hg})(^{5}\!/_{10}) = 13.85 \text{ mm Hg}$$

2. $p_{air} = (734 \text{ mm Hg})(^{5}\!/_{10}) = 367 \text{ mm Hg}$
3. $P = (762 \text{ mm Hg})(^{5}\!/_{10}) = 381 \text{ mm Hg}$
4. $V = 10$ liters (given)
5. 0.00710 gmole of water vapor (no change)
6. 0.188 gmole of dry air (no change)
7. No water condenses.

g. Conditions when the original mixture is compressed at constant temperature to 1 liter:

1. If the original mixture is compressed, condensation may occur. If the water vapor did not condense, its new partial pressure would be (27.7 mm Hg)(5/1) = 138.5 mm Hg. But the vapor pressure of water at 40°C is only 55.3 mm Hg. Therefore water condenses, and the final mixture will be saturated with water vapor at a partial pressure of 55.3 mm Hg.
2. The dry air increases in pressure as follows:

$$p_{air} = (734 \text{ mm Hg})(\tfrac{5}{1}) = 3670 \text{ mm Hg}$$

3. $P = 3670 + 55.3 = 3725$ mm Hg total pressure
4. $V = 1$ liter (given)
5. There is 1 liter of water vapor at 55.3 mm Hg and 40°C.

$$\left[(1 \text{ liter})\left(\frac{55.3}{760}\right)\left(\frac{273}{313}\right)\right]\left(\frac{1}{22.4}\right) = 0.00284 \text{ gmole water vapor}$$

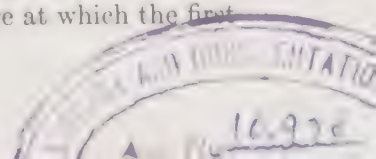
6. 0.188 gmole dry air (no change)
7. 0.0071 − 0.00284 = 0.00426 gmole H_2O condenses.

The results are summarized in Table 2-1.

Table 2-1. Answers to Example 2-9

Part	*a*	*b*	*c*	*d*	*e*	*f*	*g*
P, mm Hg	762	762	762	809.4	707.5	381	3725
V, liters	5	5.32	4.62	5	5	10	1
T, °C	40	60	20	60	20	40	40
p_{H_2O}, mm Hg	27.7	27.7	17.5	29.4	17.5	13.9	55.3
p_{air}	734.3	734.3	744.5	780	690	367	3670
gmole water vapor	0.0071	0.0071	0.00442	0.0071	0.00479	0.0071	0.00284
gmole dry air	0.188	0.188	0.188	0.188	0.188	0.188	0.188
gmole H_2O condensed	0	0	0.00268	0	0.00231	0	0.00426

The partial pressure of a vapor in a gaseous mixture may be determined by cooling at constant pressure. In this method the mixture is brought into contact with a shiny metal surface which is progressively cooled, while the surface temperature is measured. The metal surface eventually becomes clouded with small droplets of condensate. This occurs because the gaseous mixture at the metal surface is at the temperature of the surface and when the partial pressure of the vapor (which stays constant during the initial cooling because the mole fraction and total pressure do not change) equals the vapor pressure of liquid at that temperature (vapor pressure depends on temperature only), the gas becomes saturated and condensation commences. The temperature at which the first



cloudiness appears is called the *dew point.* Reference to vapor-pressure data for the liquid gives the partial pressure of the vapor in the original mixture.

The gaseous mixture of Example 2-9 has a dew point of 27.8°C because the vapor pressure of liquid water at 27.8°C is 27.7 mm Hg. Condensation would begin at that temperature in the process described in part *c*.

The principles of gas and vapor behavior expounded above are very important industrially. An interesting example of the application of these principles is the Orsat analysis. The Orsat method is the commonest method of combustion-gas analysis. Standardized apparatus is available at low cost, and the information determined by the analysis is sufficient for combustion calculations.

The method is used for hydrocarbon fuels (coal, liquefied petroleum gas, natural gas, coal gas, etc.), which are converted into oxides of carbon and hydrogen by burning in air. The following problem illustrates the chemical nature of the Orsat analysis and the significance of the data which are obtained by it.

Example 2-10. Some of the flue gas from a coal furnace is removed from the flue, cooled to room temperature, and a sample is trapped above water, in a graduated cylinder. The sample has a volume of 100 cm^3 at room temperature and atmospheric pressure. No gas dissolves in the water, since the water was previously saturated with flue-gas constituents. The sample is passed to a device in which potassium hydroxide absorbs all the carbon dioxide but no other gas and is then returned to the graduated cylinder where its volume at room temperature and atmospheric pressure is measured. A similar procedure is employed to remove oxygen with alkaline pyrogallol and carbon monoxide with cuprous chloride. The data from a certain flue-gas analysis are as follows:

Temperature	75°F
Pressure	758 mm Hg
Original volume of sample	100 cm^3
Volume after CO_2 removal	87.9 cm^3
Volume after O_2 removal	80.7 cm^3
Volume after CO removal	80.5 cm^3

Calculate the percentage analysis (by volume) of the flue gas on a dry basis (CO_2, O_2, and N_2), assuming that the 100-cm^3 sample was saturated with water vapor and contained no hydrocarbon gases.

Solution. Since the sample is saturated with water vapor, each successive reduction in volume causes condensation of water. The partial pressure of water vapor therefore remains at all times at the level corresponding to saturation at 75°F. The vapor pressure of water at 75°F = 22.2 mm Hg. We may assume that the volume occupied by the condensed water is negligible.

The percentage of CO_2 "on a dry basis" is the percentage of CO_2 in the dry gases. Therefore the volume of dry CO_2 and of total dry gases, at the same temperature and pressure, must be calculated. The partial pressure of the dry gases is 758 − 22.2 = 725.8 mm Hg. The volume of dry gases at 75°F and 725.8 mm Hg was 100 cm³. Therefore the partial volume of dry gases (at 75°F and 758 mm Hg) was (100)(725.8/758) cm³. The volume which the CO_2 and the water vapor condensed in CO_2 removal (because of volume change) occupied at 75°F and 758 mm Hg was 100 − 87.9 = 12.1 cm³. The CO_2 occupied 12.1 cm³ at 75°F and 725.8 mm Hg. Therefore the partial volume of the CO_2 (at 75°F and 758 mm Hg) was (12.1)(725.8/758) cm³. The percentage of CO_2 on a dry basis is therefore

$$(100)\left(\frac{(12.1)(725.8/758)}{(100)(725.8/758)}\right) = 12.1\%\text{v}$$

Notice that the volume change on CO_2 removal divided by the original sample volume gives the same result and that the above calculation is unnecessary. This is because the water vapor exerts the same partial pressure before and after CO_2 removal. Therefore the 12.1 cm³ of CO_2 and the 100 cm³ of dry gases are already at identical pressure (725.8 mm Hg) and temperature, and the percentage of the dry-gas volume occupied by CO_2 must be 12.1%v.

Similarly, it may be concluded that the oxygen occupied

$$87.9 - 80.7 = 7.2\%$$

of the original volume, and the CO occupied 80.7 − 80.5 = 0.2%v. Since we are assuming perfect gases, volume per cent, as obtained above, is equal to mole per cent.

Gas-law Limitation. Throughout the chapter we have referred to the fact that no real gases obey the perfect-gas law exactly. You may well ask why so much emphasis has been placed on it. There are two reasons for this. The first reason is that for most gases, when the pressure is 10 atm or less, the perfect-gas law may be used with confidence to give engineering accuracy. The upper limit of its use is, however, dependent on both the gas and the desired accuracy of the calculations. A discussion of these limitations is not within the scope of this text.

The other reason for the emphasis on the perfect-gas law is that the methods of making calculations for gases are well illustrated by the use of this law. Calculations for real gases sometimes involve the use of quite complex equations. The study of these equations is best deferred until a course in physical chemistry is taken. The use of the more complex equations complicates the mathematical details, but the principles of the calculations remain unchanged.

PROBLEMS

2-1. Carbon tetrachloride has the formula CCl_4.

a. What are the atomic weights of carbon and chlorine?

b. One molecule contains how many atoms of carbon and chlorine?

c. What is the ratio of the weight of chlorine to the weight of carbon in one molecule?

d. 6.06×10^{23} molecules comprise 1 gmol of CCl_4. What is the weight of 1 gmole?

e. What is the weight of carbon and chlorine in 1 gmole?

f. One poundmole contains 454 gmole. What is the weight of 1 lbmole?

g. What is the weight of carbon and chlorine in 1 lbmole?

h. How many poundatoms of carbon and poundmoles of chlorine are necessary to form 1 lbmole of CCl_4?

2-2. How many poundmoles are in 100 lb of each of the following:

a. $CaCO_3$ *b.* H_2 *c.* HCl *d.* MgO *e.* $H_2S_2O_7$

2-3. Find the percentage by weight of carbon in

a. CH_4 *b.* CO *c.* CO_2 *d.* $CaCO_3$ *e.* CCl_4

2-4. A compound consists of 62.4%w Ca and 37.6%w C.

a. How many poundatoms of carbon are in 100 lb of the compound?

b. How many poundatoms of calcium are in 100 lb of the compound?

c. What is the ratio of poundatoms of carbon to poundatoms of calcium?

d. What is the simplest chemical formula that can be written for the compound?

2-5. A compound with a molecular weight of 138.7 contains 52.3%w C, 4.36% H, 20.19% N, and 23.08% O. What is its empirical formula?

2-6. A compound whose formula is XCl_2, soluble in water, is known to form an insoluble sulfate. In a quantitative analysis, 100 ml of a solution of XCl_2 is treated with an excess of H_2SO_4, and 2.36 g of dry XSO_4 is obtained. A separate analysis shows that 0.01 gmole of Cl_2 can be obtained from 100 ml of solution. What is the atomic weight of X, according to this analysis?

2-7. A mixture of NaCl and NaOH contains 40%w Na. What are the weight percentages of NaCl and NaOH in the mixture?

2-8. In the neutralization reaction

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

a. What are the relative weights of the molecules of NaOH, H_2SO_4, Na_2SO_4, and H_2O?

b. When one molecule of H_2SO_4 reacts, how many molecules of NaOH react, and how many molecules of Na_2SO_4 and H_2O are formed?

c. When 6.06×10^{23} molecules of H_2SO_4 (1 gmole) react, how many molecules of NaOH react, and how many molecules of Na_2SO_4 and H_2O are formed?

d. When 1 gmole of H_2SO_4 reacts, how many grammoles of NaOH react, and how many grammoles of Na_2SO_4 and H_2O are formed?

e. When 454 gmole (1 lbmole) of H_2SO_4 reacts, how many poundmoles of NaOH react, and how many poundmoles of Na_2SO_4 and H_2O are formed?

f. What are the weights of H_2SO_4 and NaOH reacting and of Na_2SO_4 and H_2O formed when 1 kgmole of H_2SO_4 reacts?

2-9. One hundred grams of chlorine gas is mixed with 10 g of hydrogen gas.

a. How many grammoles of chlorine gas are present?

b. How many grammoles of hydrogen gas are present?

c. How many moles of mixed gas are present?

d. The number of moles of chlorine gas is what fraction of the total number of moles present?

e. The number of moles of hydrogen gas is what fraction of the total number of moles present?

f. What is the sum of the two mole fractions?

Upon ignition by a spark, the reaction

$$H_2 + Cl_2 \rightarrow 2HCl$$

takes place. Assuming complete reaction,

g. How many moles of HCl are formed?

h. What weight of HCl is formed?

i. What are the limiting and excess reactants?

j. What is the "theoretically required" amount of the excess reactant, i.e., the amount necessary to react with all the limiting reactant?

k. What is the per cent excess of the excess reactant?

l. What is the percentage conversion of the excess reactant?

2-10. A coke is known to contain 90%w C and 10%w noncombustible ash. Depending on conditions, the carbon can burn to either CO or CO_2.

a. How many poundmoles of oxygen are theoretically required to burn 100 lb of coke completely (to CO_2)?

b. If 50% excess oxygen is supplied and if 80% of the carbon present burns to CO_2, the rest going to CO, how many moles of gases (O_2, CO, and CO_2) are present at the end of combustion?

c. What are the mole fractions of the three gases in the final mixture?

d. What are the weights of the three gases in the final mixture?

e. What fractions of the total weight of gases are the weights of each of the three constituents?

2-11. Calculate the density in lb/ft^3 of a mixture of 40%v CH_4 and 60%v H_2 at 50°C and 4.5 atm total pressure.

2-12. Pyrites (FeS_2) is often used as a source of sulfur gases. The usually desired reaction is

$$4FeS_2 + 15O_2 \rightarrow 2Fe_2O_3 + 8SO_3$$

However, the reaction

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

occurs simultaneously, and most of the sulfur is oxidized to SO_2 rather than SO_3. Catalytic converters are required to oxidize this SO_2 to SO_3. An analysis of exit gases from a pyrites burner in which FeS_2 was burned with dry air shows a ratio of 4:2:1 for SO_2:O_2:SO_3. Choosing a convenient basis of 7 moles of this mixture,

a. How many moles of oxygen were used to obtain the SO_3?

b. How many moles of oxygen were used to obtain the SO_2?

c. How many moles of oxygen must have been supplied originally?

d. How many moles of oxygen would have been used if all the sulfur had gone to SO_2?

e. What is the excess number of moles of oxygen?

f. What is the per cent excess of oxygen?

g. How many moles of FeS_2 must have been burned to furnish the sulfur present in the gas?

2-13. Ethane, C_2H_6, reacts with pure oxygen to form water and CO_2. If 3 mole of C_2H_6 and 12 mole of oxygen are mixed, and 80% of the ethane reacts,

a. How many moles of C_2H_6, O_2, H_2O, and CO_2 are present in the final mixture?
b. What are the mole fractions of the four gases?
c. What are the weights of the gases?
d. What are the weight fractions of the gases?
e. What is the excess number of moles of oxygen?
f. What is the per cent excess of oxygen?

2-14. Sea water has an average specific gravity of about 1.03. A rough analysis shows that it contains 2.8%w NaCl, 0.50% $MgCl_2$, and 0.0085% NaBr. How many tons of chlorine, magnesium, and bromine could be obtained from these three salts in a cubic mile of sea water?

2-15. Benzene, C_6H_6, has a specific gravity of 0.872 at 25°C, and ethylene dichloride, $C_2H_4Cl_2$, has a specific gravity of 1.246.

a. How many pounds of each would be required to make up 100 lb of a solution of 20%m C_6H_6 and 80%m $C_2H_4Cl_2$?

b. If the final volume of the mixture is equal to the sum of the volumes of the two constituents before mixing, what is the density of the mixture in lb/ft^3?

2-16. If a substance at 0°F is heated to 100°F,

a. What are the initial and final temperatures in °C, °R, and °K?
b. What is the change in temperature in C°, R°, and K°?
c. Calculate the change in temperature in C°, R°, and K° when the temperature of a body rises 100 F°; show that this calculation can be made even when actual temperatures are unknown.

2-17. The Reaumur temperature scale reads 0°Reaumur at the freezing point of water and 80°Reaumur at its boiling point.

a. What temperature on this scale corresponds to absolute zero?
b. What temperature corresponds to 0°F?
c. At what temperature are the Fahrenheit and Reaumur temperatures the same numerically?

2-18. Carbon tetrachloride, sometimes used in manometers for measuring pressures or pressure differences, has a density of 1.584 g/cm^3 at 25°C. What "head" (in feet) of CCl_4 would correspond to a pressure of 1 atm?

2-19. A substance has a vapor pressure of 1000 mm Hg at a given temperature. What is its pressure, expressed in

a. atm?
b. psig, if atmospheric pressure is 14.7 psia?
c. lb/ft^2?
d. in. H_2O?

2-20. What pressure in atmospheres is equivalent to 1 megabar? Show the conversion, using

$$1 \text{ atm} \approx \frac{14.7 \text{ lb}_f}{\text{in.}^2}$$

$$1 \text{ bar} \approx \frac{1 \text{ dyne}}{\text{cm}^2}$$

$$1 \text{ dyne} \approx \frac{1 \text{ (g)(cm)}}{\text{sec}^2}$$

$$\text{"mega"} = 10^6$$

2-21. Show that the two values of R, 0.08206 (atm)(liter)/(gmole)(°K) and 1545 $(lb/ft^2)(ft^3)/(lbmole)(°R)$, are consistent.

2-22. Convert a diffusion or coefficient of 0.5 $lb/(hr)(ft^2)(atm)$ to $g/(sec)(cm^2)(mm Hg)$.

2-23. The equation for pressure drop due to friction for fluids flowing in a pipe is

$$\Delta p = \frac{2fL\rho u^2}{g_c D}$$

where Δp = pressure drop, lb_f/ft^2
u = velocity, ft/sec
L = length of tube
ρ = density of fluid
g_c = a constant, 32.17 $(ft)(lb_m)/(sec^2)(lb_f)$
D = diameter of pipe

What are the units of the "friction factor" f? Use convenient engineering units for L, ρ, u, and D.

2-24. How many grammoles of nitrogen are present in 100 liters at these conditions?

a. 0°C and 1 atm?
b. 0°F and 1 atm?
c. 100°C and 10 mm Hg?
d. 100°F and 100 psia?
e. Are the answers in *a*, *b*, *c*, and *d* changed if any other perfect gas is substituted for nitrogen?

2-25. How many poundmoles of nitrogen are present in 1000 ft^3 at these conditions:

a. 0°C and 1 atm?
b. 0°F and 1 atm?
c. 100°C and 10 mm Hg?
d. 100°F and 100 psia?

2-26. One hundred grams of a gas mixture is known to contain 72.48 g N_2, 7.34 g O_2, and 20.18 g CO_2.

a. How many grammoles of nitrogen are there?
b. How many grammoles of oxygen are there?
c. How many grammoles of CO_2 are there?
d. What is the total number of moles?
e. What is the mole fraction of nitrogen (ratio of moles of nitrogen to total moles)?
f. What is the mole fraction of oxygen?
g. What is the mole fraction of CO_2?
h. What is the sum of the mole fractions?
i. What is the weight fraction of nitrogen?
j. What is the weight fraction of oxygen?
k. What is the weight fraction of CO_2?
l. What is the sum of the weight fractions?
m. Is weight fraction equal to mole fraction?
n. What is the quotient of total weight divided by number of moles? This is the average molecular weight.
o. What volume would the mixture occupy at 20°C and 1 atm?
p. What volume would the nitrogen alone occupy at 20°C and 1 atm?
q. What volume would the oxygen alone occupy at 20°C and 1 atm?
r. What volume would the CO_2 alone occupy at 20°C and 1 atm?
s. What is the sum of the three pure component volumes?
t. What is the ratio of the volume of nitrogen at 20°C and 1 atm to the total volume at 20°C and 1 atm?
u. Is volume fraction equal to mole fraction?

v. What would be the pressure of the nitrogen at 20°C if it alone occupied the total volume of the mixture?

w. What would be the pressure of the oxygen at 20°C and the total volume?

x. What would be the pressure of the CO_2 at 20°C and the total volume?

y. What is the sum of the partial pressures?

z. What is the ratio of the partial pressure of nitrogen at 20°C and the total volume to the total pressure of the mixture?

aa. Is pressure fraction equal to mole fraction?

bb. If the nitrogen alone were at 0°C and 1 atm, what would its volume be?

cc. What would be the ratio of the volume of nitrogen at 0°C and 1 atm to that of the total mixture at 20°C and 1 atm?

dd. Why is the answer in *cc* not equal to the mole fraction of nitrogen in the original mixture?

ee. What would be the pressure of the nitrogen alone at the total volume of the mixture as determined above and 0°C?

ff. What is the ratio of the pressure of nitrogen at 0°C and the total volume to the pressure of the mixture at 20°C and 1 atm?

gg. Why is the answer in *ff* not equal to the mole fraction of nitrogen in the original mixture?

2-27. Fifty cubic feet of oxygen at 14.7 psig and 0°F is mixed with 21 lb of nitrogen at 20°C and 740 mm Hg, and the resulting mixture is brought to 10°C and 1 atm. What is the partial pressure of oxygen (in atm) in the final mixture?

2-28. The gases flowing through a pipe contain 4% O_2 by volume. The rate of flow is 1000 ft^3/min. It is desired to increase the oxygen content so that the gases leaving the pipe will contain 8% by volume.

a. Calculate the rate of addition of pure oxygen to the mixture.

b. If the change in composition is caused by adding air (21%v O_2, 79% N_2), what is the rate of addition of air?

c. With the data available, what must be assumed in making the above calculations?

2-29. A mixture of nitrogen and CO_2 at 30°C and 2 atm has an average molecular weight of 31.

a. What is the partial pressure of the nitrogen?

b. What is the volume of 10 lb of the mixture?

2-30. In some industries conditions other than 1 atm pressure and 0°C are chosen as "standard conditions" for gas mixtures. These are sometimes referred to as "commercial standard conditions" or "industrial standard conditions." One such set of conditions is 60°F, 30 in. Hg, with the gas saturated with water vapor. What is the "standard molar volume" (volume to contain 1 lbmole of dry gas) under these conditions?

2-31. One hundred pounds per hour of an organic ester of formula $C_{19}H_{36}O_2$ is being hydrogenated to $C_{19}H_{38}O_2$. The process runs continuously. The company purchases its hydrogen in cylinders of 10-ft^3 capacity, and the pressure initially is 1000 psia at room temperature of 70°F. If the company buys a week's supply of hydrogen at one time,

a. How many cylinders should it order each week?

b. What simplifying assumptions are made to solve this problem?

2-32. Sulfur dioxide reacts with pure oxygen to form SO_3. If the reaction is carried out with twice as much oxygen as necessary for complete oxidation (100% excess) but under such low temperature and pressure that the reaction goes only 60% to completion (based on the limiting reactant),

a. Calculate the mole fractions of SO_2, O_2, and SO_3 in reactants and products.
b. Calculate the weight fractions of the three gases in reactants and products.
c. Calculate the average molecular weights of reactants and products.
d. Calculate the partial pressures of the products if the total pressure is 2 atm.
e. If the products were cooled to 70°F and the pressure reduced to 735 mm Hg, what volume of gas would be obtained from 100 lb SO_2?

2-33. Carbon dioxide dissociates, at high temperatures, according to the following equation:

$$2CO_2 \rightleftharpoons 2CO + O_2$$

At 3000°C and 1 atm CO_2 is 40% dissociated. If 5 liters of CO_2 at 20°C and 1 atm is heated to 3000°C at constant pressure, what volume of gas will result?

2-34. Certain gases have a tendency to associate. One example, familiar to all physical chemists, is the equilibrium between nitrogen dioxide and nitrogen tetroxide:

$$2NO_2 \rightleftharpoons N_2O_4$$

In one case 26.6 ft³ of NO_2 at 685 mm Hg and 25°C is allowed to stand at constant temperature and volume until equilibrium is reached, at which time the pressure is 500 mm Hg. Calculate the partial pressure of N_2O_4 in the final mixture.

2-35. One hundred cubic feet of a saturated mixture of air and water vapor exists at 40°C and 750 mm Hg. No liquid water is present. Calculate and tabulate the following:

(1) Partial pressure of water vapor (mm Hg)
(2) Partial pressure of air
(3) Total pressure
(4) Final volume
(5) Poundmoles of water vapor in the final mixture
(6) Poundmoles of air in the final mixture
(7) Poundmoles of water condensed
(8) Temperature

for each of the following cases:

a. Initial values.
b. The original mixture is heated at constant pressure to 60°C.
c. The original mixture is cooled at constant pressure to 20°C.
d. The original mixture is heated at constant volume to 60°C.
e. The original mixture is cooled at constant volume to 20°C.
f. The original mixture is expanded at constant temperature to 200 ft³.
g. The original mixture is compressed at constant temperature to 50 ft³.

Data: Vapor pressures of water are

20°C; 17.5 mm Hg
40°C; 55.3 mm Hg
60°C; 149 mm Hg

2-36. Air with a moisture content of 0.02 lb H_2O/lb dry air is originally at a temperature of 100°F and a total pressure of 1 atm. This air is cooled at constant pressure to 80°F and then compressed isothermally to 5 atm. What is the ratio of final to initial volume? The vapor pressure of water at 100°F is 0.949 psia and at 80°F it is 0.507 psia.

2-37. At 153°F and 1 atm total pressure a mixture of water vapor and air (not

saturated) has a density of 0.0615 lb/ft³. It is compressed isothermally to 3 atm, and some water condenses out. The remaining saturated gas has a density of 0.1878 lb/ft³. Calculate the following:

a. The vapor pressure of water in lb/in.² absolute at 153°F

b. The pounds of water condensed from 1 lbmole of total gas initially present

2-38. A mixture of toluene, C_7H_8, and air is passed through a cooler where some of the toluene is condensed. One thousand cubic feet of gases enters the cooler per hour at a temperature of 100°C and a pressure of 100 mm Hg gauge. The partial pressure of toluene in this mixture is 300 mm Hg. Seven hundred and twenty cubic feet of gas mixture leaves the cooler per hour at a barometric pressure of 740 mm Hg and a temperature of 50°C. Calculate the pounds of toluene removed per hour in the cooler.

2-39. Air enters a compressor at 1 atm pressure containing 0.01 mole H_2O/mole dry air. The air leaving the compressor is at 100 atm and the initial temperature. At the initial temperature and 1 atm pressure, air can contain a maximum of 0.02 mole H_2O/mole dry air. How many pounds of water are condensed in the compressor per mole of dry air passing through?

2-40. A producer gas, having an Orsat analysis of 6.6%v CO_2, 20.8% CO, 0.6% O_2, 11.4% H_2, 1.9% CH_4, and the rest N_2, enters a compressor and cooler at a pressure of 735 mm Hg and a temperature of 250°F. The partial pressure of water in this gas is 200 mm Hg. The gas is compressed and cooled for storage to 150 psia and 70°F. On the basis of 100 lbmole of dry gas entering, how many pounds of liquid water are condensed out in this operation?

2-41. Propane, C_3H_8, is burned with 60% excess air. All the hydrogen burns. Eighty per cent of the carbon burns to CO_2 and 20% to CO. Calculate the following:

a. The volumetric (wet) analysis of the exit gases

b. The Orsat analysis of the exit gases

2-42. An analyst attempts to analyze air (79%v N_2, 21% O_2) with an Orsat apparatus containing Hg and does not add a drop of H_2O above the Hg to saturate the sample. At the temperature of the experiment the vapor pressure of water is 1.422 in. Hg. The original sample contains 4.5%v H_2O, which is not sufficient for saturation. Barometric pressure is 720 mm Hg. In the analysis, oxygen is absorbed first, and the remaining gas is nitrogen. At any point in the analysis when the concentration of water vapor exceeds the saturation value, the excess water will condense. What analysis is obtained in this case?

2-43. At 43°C, benzene, C_6H_6, exerts a vapor pressure of 200 mm Hg. If a mixture of 20%m C_6H_6 in nitrogen at 43°C and 800 mm Hg is isothermally compressed until the final gaseous volume is 20% of the original volume, what weight of C_6H_6 is condensed from each 1000 ft³ of original mixture?

2-44. Methane burns to form CO_2 and H_2O. If 1 lbmole of CH_4 is burned with pure oxygen, an excess of 10% O_2 above that for complete combustion being supplied, and the resulting gas mixture is cooled and thoroughly dried, calculate the following:

a. Volume of dry exit gas at 70°F and 750 mm Hg

b. Partial pressure of oxygen in the mixture of dry products

c. Weight of water removed in drying

2-45. Pure methane is completely burned with air. The outlet gases from the burner, which contain no oxygen, are passed through a cooler where some of the water is removed. In the gases leaving the cooler, the mole fraction of nitrogen is 0.8335. Calculate the following:

a. The analysis of the gases leaving the cooler (%m CO_2, H_2O, N_2).

b. The pounds of H_2O condensed/mole CH_4 burned.

c. Average molecular weight of the gases leaving the cooler. If the cooler gases are at 130°F and 20 psia,

d. What are the partial pressures of the components?

e. What are the partial volumes per mole of CH_4?

f. To what temperature can the gas be cooled at constant pressure before more condensation will occur?

g. To what pressure can the gas be compressed at constant temperature before more condensation will occur?

Chapter 3

MATERIAL BALANCES

In the early part of the seventeenth century many learned men believed that earth, mercury, sulfur, and salt were the elements of which all matter was composed. A certain Belgian physician, Jan Baptista Van Helmont, took issue with this belief. He planted a 5-lb willow tree in 200 lb of earth, watered it for 5 years, then weighed the tree and the earth separately. The weight of the earth had not changed, but the tree had gained 164 lb. He concluded that water, not earth, was an element, since it, and not earth, had been transformed into the substance of the tree. This was a commendable approach, for a time when men preferred to philosophize rather than to experiment. It is one of the earliest applications of a theory which was later known as the law of conservation of mass. The law stated that matter could not be created or destroyed. This idea was so universal that no attempt was made to prove it; it was simply taken for granted. On the first occasion when it could have been doubted, no one thought to dispute it but simply explained the facts in a way which left the law inviolate. This occasion arose in connection with the phlogiston theory, proposed by Georg Ernst Stahl before the year 1700. The phlogiston theory stated that all combustible substances possessed one component in common which escaped in the act of burning. Stahl named the component "phlogiston," meaning "fire substance." When it was pointed out that the calx (oxide) of a metal weighed more than the original metal, Stahl concluded that phlogiston had a negative weight, as evidenced by its upward flight during combustion.

In spite of the fact that the ethereal, illusive phlogiston was the only known example of negative weight, the theory flourished for nearly one hundred years, until Antoine Laurent Lavoisier made the first completely rigorous application of the law of conservation of mass to a chemical reaction. In 1789, he sealed a quantity of tin into an air-filled glass vessel and heated the system until the calx was formed. He noted that air rushed in when the seal was broken. The increase in weight of the entire system was exactly equal to the increase in weight of the tin, and he therefore concluded that the metal had combined with part of the air.

The phlogiston theory and the concept of negative weight were forever discredited. His work paved the way for quantitative analysis and the chemical equation.

The law of conservation of mass was accepted as self-evident until recent times, when Albert Einstein showed the relationship between matter and energy and indicated that a decrease in mass did indeed occur when a chemical reaction evolved energy. To be exact, we should state that a chemical reaction follows the law of conservation of mass and energy.

For all "ordinary" processes (exclusive of nuclear reactions) the change in mass is negligible, and a mass (or "material") balance may be written. The equation for material balance is

$$\text{Input} - \text{output} = \text{accumulation}$$

It may be written for the total material involved, for any compound whose quantity is not changed by chemical reaction, and for any chemical element whether or not it has participated in a chemical reaction. It may be written for one piece of equipment, or "around" several pieces of equipment, or around an entire process. It may be used to calculate an unknown quantity directly, to check the validity of experimental data, or to express one or more of the independent relationships between the unknown quantities in a particular problem situation.

For material-balance purposes, industrial processes may be classified as steady- or unsteady-state processes and as batch or continuous processes. (The chemical engineer also classifies them as unit processes and unit operations for reasons which will be discussed in subsequent chapters.)

A steady-state process is one in which there is no change in conditions (pressure, temperature, composition) or rates of flow with time at any given point in the system. All other processes are unsteady-state.

In a batch process, a given quantity of reactants is placed in a container, and by chemical and/or physical means, a change is made to occur. At the end, the container, or adjacent ones to which material may have been transferred, holds the product or products. All batch processes are unsteady-state.

In a continuous process, reactants are continuously fed to a piece of equipment or to several pieces in series, and products are continuously removed from one or more points.

A continuous process may or may not be steady-state. A power plant, for example, operates continuously. However, because of the wide variation in power demand between peak and slack periods, there is an equally wide variation in the rate at which the coal is fired. For this reason, power-plant problems require the use of average data over long periods of time.

Many chemical-engineering processes may be assumed to be steady-state (and continuous). If they are truly steady-state, the instantaneous values of flow rates, compositions, etc., are used in problem solution. In these problems there is no accumulation in any piece of equipment, and the law of conservation of matter is written as

$$\text{Input} = \text{output}$$

The rest of this chapter illustrates the use of the material balance. The suggested steps for problem solution, mentioned briefly in Chap. 1, are elaborated and listed here. Refer to the list frequently. It is supposed to be habit-forming.

1. Read the entire problem carefully.
2. Draw a picture of the equipment, indicating all streams of material which enter and leave. Any piece of equipment may be represented merely as a box or enclosure, since the actual physical shape has no bearing on the calculations. Streams which do not cross an imaginary surface surrounding the equipment need not be shown. This would apply to some streams between intermediate pieces of equipment when the material balance is being made around several pieces of equipment combined.
3. Label all pieces of equipment and streams of importance with the data pertaining to them. Include pressure, temperature, composition, rates of flow, etc. Do not feel, however, that every item of data must be used. Extraneous data are frequently available.
4. Consider the entire problem, and decide what quantities will have to be calculated in order to achieve the final solution.
5. Choose the basis or bases.
6. Write any chemical equations necessary.
7. Solve the problem, using complete units and labels.
8. Check the answer qualitatively as indicated in the section on qualitative considerations in Chap. 1.

Basis: Quantities may not be added or subtracted unless they are on the same basis. In a particular problem, different bases may be chosen for various parts of the calculations. A basis serves only to establish equivalent amounts of material; it does not "permit" or "forbid" a problem solution. However, the difficulty of the problem often depends upon the basis chosen, and therefore the choice should not be made arbitrarily. The following example shows that the character of the solution is influenced by the basis.

Example 3-1. One ton of a 25 %w solution of $NaNO_3$ is concentrated to saturation at 100°C by evaporation. The solution is then cooled to 20°C. The crystals of $NaNO_3$ are removed by filtration. One-tenth pound of solution adheres to each pound of crystals. When the crystals

are dried, the $NaNO_3$ in the adhering solution is deposited on the crystals. The solubility of $NaNO_3$ is 1.76 lb/lb H_2O at 100°C and 0.88 lb/lb H_2O at 20°C. Calculate (*a*) the amount of water evaporated to achieve saturation at 100°C and (*b*) the total weight of $NaNO_3$ obtained. Do the calculation using a basis of 1 ton of original solution and then repeat using a basis of 100 lb of water evaporated for part *a* and a basis of 100 lb of $NaNO_3$ obtained for part *b*.

Solution 1

a. Amount of water evaporated in concentrating to saturation at 100°C

Basis: 1 ton of original solution

$$(2000 \text{ lb orig soln})\left(\frac{25 \text{ lb } NaNO_3}{100 \text{ lb orig soln}}\right) = 500 \text{ lb } NaNO_3$$

$$(500 \text{ lb } NaNO_3)\left(\frac{2.76 \text{ lb ``100°C soln''}}{1.76 \text{ lb } NaNO_3}\right) = 784 \text{ lb ``100°C soln''}$$

$$2000 - 784 = 1216 \text{ lb } H_2O \text{ evap}$$

b. Total weight of $NaNO_3$ obtained

Basis: 1 ton of original solution. Since the solubility of $NaNO_3$ at 20°C is one-half that at 100°C, 250 lb of crystals form.

$$(250 \text{ lb crystals})\left(\frac{0.1 \text{ lb ``20°C soln''}}{\text{lb crystals}}\right)\left(\frac{0.88 \text{ lb } NaNO_3}{1.88 \text{ lb ``20°C soln''}}\right)$$

$$= 11.7 \text{ lb } NaNO_3 \text{ in adhering soln}$$

$$250 + 11.7 = 261.7 \text{ lb } NaNO_3 \text{ obtained}$$

Solution 2

a. Amount of water evaporated in concentrating to saturation at 100°C

Basis: 100 lb H_2O evaporated. Let x = amount of $NaNO_3$ in original solution per 100 lb of H_2O evaporated.

$$(x \text{ lb } NaNO_3)\left(\frac{100 \text{ lb orig soln}}{25 \text{ lb } NaNO_3}\right) = 4x \text{ lb orig soln}$$

$$4x - 100 = \text{lb ``100°C soln''}$$

$$\frac{x}{4x - 100} = \frac{1.76}{2.76} = \frac{\text{lb } NaNO_3}{\text{lb ``100°C soln''}}$$

$$x = 41.2 \text{ lb } NaNO_3$$

$$(4)(41.2) = 164.8 \text{ lb orig soln}$$

$$(2000 \text{ lb orig soln})\left(\frac{100 \text{ lb } H_2O \text{ evap}}{164.8 \text{ lb orig soln}}\right) = 1216 \text{ lb } H_2O \text{ evap}$$

b. Total weight of $NaNO_3$ obtained

Basis: 100 lb of $NaNO_3$ obtained. Let x = weight of crystals at 20°C per 100 lb of $NaNO_3$ obtained.

$$(x \text{ lb crystals}) \left(\frac{0.1 \text{ lb "20°C soln"}}{\text{lb crystals}}\right) \left(\frac{0.88 \text{ lb } NaNO_3}{1.88 \text{ lb "20°C soln"}}\right)$$
$$= (100 - x) \text{ lb } NaNO_3 \text{ in adhering soln}$$
$$x = 95.5 \text{ lb crystals} \cdot$$

Since the solubility of $NaNO_3$ at 100°C is twice that at 20°C, the crystals must have formed from an amount of "100°C soln" that contained 191 lb of $NaNO_3$:

$$(191 \text{ lb } NaNO_3) \left(\frac{100 \text{ lb orig soln}}{25 \text{ lb } NaNO_3}\right)$$
$$= 764 \text{ lb of orig soln contained 191 lb of } NaNO_3$$
$$(200 \text{ lb orig soln}) \left(\frac{100 \text{ lb } NaNO_3 \text{ obtained}}{764 \text{ lb orig soln}}\right) = 262 \text{ lb } NaNO_3 \text{ obtained}$$

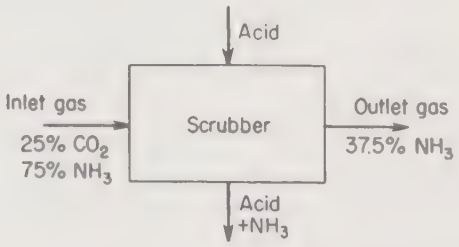
This is the same answer (to slide-rule accuracy) as in Solution 1.

KEY COMPONENT

The primary task in preparing a material balance is to develop the quantitative relationships between the streams. The primary factors, therefore, are those which "tie" the streams together. An element, compound, or unreactive mass (like the ash in a coal furnace) that enters or leaves in a single stream is so convenient for this purpose that it may be considered a "key" to the calculations. In this text we refer to such a material as a *key component.*

Example 3-2. A gas mixture containing 25%v CO_2 and 75%v NH_3 is being scrubbed with an acid solution to remove the ammonia. The resulting gas mixture contains 37.5%v NH_3. What percentage of the original ammonia has been removed, assuming that the CO_2 remains unaffected and that no part of the acid solution vaporizes?

Solution



Basis: 100 mole of inlet gas. The 25 mole of CO_2 passes through the process unabsorbed and leaves in the exit gas stream. The CO_2 is a key component for obtaining equivalent quantities of inlet and outlet gases.

Since the CO_2 is 62.5%m of the outlet gas, there must be

$$(25 \text{ mole } CO_2)\left(\frac{37.5 \text{ mole } NH_3 \text{ leaving}}{62.5 \text{ mole } CO_2 \text{ leaving}}\right) = 15 \text{ mole } NH_3 \text{ leaving}$$

and

$$75 - 15 = 60 \text{ mole of } NH_3 \text{ absorbed}$$

$$(^{60}/_{75})(100) = 80\% \text{ of } NH_3 \text{ absorbed}$$

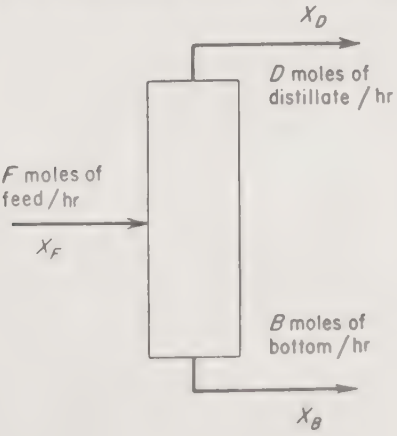
SIMULTANEOUS EQUATIONS

There are two distinctly different ways to solve algebraic problems. The first way is to write an equation involving only one unknown quantity, solve it, use the answer in writing an equation involving the next unknown quantity, solve it, and repeat the procedure until all unknowns have been calculated. Each succeeding equation, as it brings in one more unknown, also expresses one more problem fact or relationship. In the step-by-step procedure of this "consecutive-equation" approach, the calculator follows a definite path of his own devising. In this approach he is particularly helped by recognizing key components.

By contrast, it is often possible (and sometimes necessary) to write a sufficient number of independent simultaneous equations and solve them in any order. In this case also, the total number of equations must equal the total number of unknowns.

Example 3-3. One hundred mole per hour of a 40%m solution of ethylene dichloride in toluene is fed into the middle of a distillation column. There is no net accumulation in the column; 100 mole/hr of total material leaves in two streams, an overhead or "distillate" stream and a "bottoms" stream. The distillate stream contains 95%m ethylene dichloride and the bottoms stream contains 10%m ethylene dichloride. What is the rate of flow of each stream?

Solution. x refers to the mole fraction of ethylene dichloride in the



particular stream.

A total material balance (in moles) gives

$$F = D + B$$

and an ethylene dichloride balance (in moles) gives

$$Fx_F = Dx_D + Bx_B$$

Substituting the known values,

$$100 = D + B$$

and

$$(100)(0.40) = (D)(0.95) + (B)(0.10)$$

Solving simultaneously, $D = 35.3$ mole/hr and $B = 64.7$ mole/hr.

We could also have written a toluene balance:

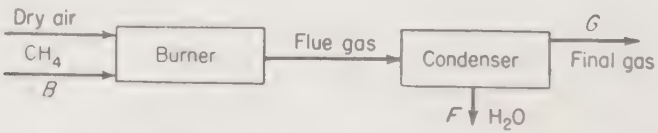
$$(0.60)(100) = 0.05D + 0.90B$$

Note that any one of the three equations can be derived from the other two. Therefore there are only two independent equations.

The simultaneous-equation approach has always had a great appeal for students since it seems much easier simply to write equations until a sufficient number have been accumulated than it does to plan a step-by-step solution. This opinion leads students to start a problem by first writing as many equations as possible. If this is done without a real analysis of the problem, extraneous quantities of no significance may be introduced. The fact is that simultaneous equations are not a panacea for problem solvers; they are essential in many problems but when they are not essential they offer no particular advantage. Following is an example of what might occur if the "blind-faith" method of writing equations indiscriminately were employed.

Example 3-4. Pure methane (CH_4) is burned with dry air, and the resulting gaseous mixture is passed through an apparatus which removes most of the water vapor by condensing it to liquid water. The remaining gas is analyzed by the Orsat method and found to contain 8.21% CO_2, 0.91% CO, 5.02% O_2, and 85.86% N_2. How many poundmoles of dry air were used per poundmole of CH_4?

Solution Attempt



Basis: 100 mole of air. Let B = mole of CH_4, F = mole condensed H_2O, and G = mole final gas.

Nitrogen balance:

$$(100 \text{ mole air})\left(\frac{79 \text{ mole } N_2}{100 \text{ mole air}}\right) = (G \text{ mole final gas})\left(\frac{y \text{ mole } N_2}{\text{mole final gas}}\right) \qquad 2 \text{ unknowns}$$

Carbon balance:

$$(B \text{ mole } CH_4)\left(\frac{1 \text{ mole C}}{\text{mole } CH_4}\right) = (G \text{ mole final gas})\left(\frac{x \text{ mole C}}{\text{mole final gas}}\right) \qquad 4 \text{ unknowns}$$

Oxygen balance:

$$(100 \text{ mole air})\left(\frac{21 \text{ mole } O_2}{100 \text{ mole air}}\right) = (F \text{ mole } H_2O)\left(\frac{0.5 \text{ mole } O_2}{\text{mole } H_2O}\right) + (G \text{ mole final gas})\left(\frac{z \text{ mole } O_2}{\text{mole final gas}}\right) \qquad 6 \text{ unknowns}$$

Hydrogen balance:

$$(B \text{ mole } CH_4)\left(\frac{2 \text{ mole } H_2}{\text{mole } CH_4}\right) = (F \text{ mole } H_2O)\left(\frac{1 \text{ mole } H_2}{\text{mole } H_2O}\right) + (G \text{ mole final gas})\left(\frac{w \text{ mole } H_2}{\text{mole final gas}}\right) \qquad 7 \text{ unknowns}$$

Total material balance:

$$(100 \text{ mole air})\left(\frac{28.9 \text{ lb air}}{\text{mole air}}\right) + (B \text{ mole } CH_4)\left(\frac{16 \text{ lb } CH_4}{\text{mole } CH_4}\right) = (F \text{ mole } H_2O)\left(\frac{18 \text{ lb } H_2O}{\text{mole } H_2O}\right) + (G \text{ mole final gas})\left(\frac{v \text{ lb final gas}}{\text{mole final gas}}\right) \qquad 8 \text{ unknowns}$$

At this point we might continue to try to find relationships to express as equations, or we might try to analyze the problem more carefully. The proper approach is to analyze the problem *first*. In this case an analysis would show that the water cannot be tied down by the information given and that it should be excluded from any equations. We might then have let G be the moles of dry final gas and written the equations as follows:

Nitrogen balance:

$$(100 \text{ mole air})\left(\frac{79 \text{ mole } N_2}{100 \text{ mole air}}\right) = (G \text{ mole dry final gas})\left(\frac{85.86 \text{ mole } N_2}{100 \text{ mole dry gas}}\right)$$

Solving, $G = 92$ mole dry final gas

Carbon balance:

$$(B \text{ mole } CH_4)\left(\frac{1 \text{ mole C}}{\text{mole } CH_4}\right) = (92 \text{ mole dry final gas})\left(\frac{(8.21 + 0.91) \text{ mole C}}{100 \text{ mole dry gas}}\right)$$

Solving,
$$B = 8.39 \text{ mole } CH_4$$

and
$$\frac{100}{8.39} = \frac{11.92 \text{ mole air}}{\text{mole } CH_4}$$

It may, of course, happen that an indiscriminate approach might lead to a solution. For example, we might have noticed after writing the first nitrogen and carbon balances that we could divide one into the other and solve the problem since the ratio of mole N_2:mole C is known from the Orsat analysis. But we should have failed to gain an appreciation of the roles of nitrogen and carbon as key components. Such an appreciation would be valuable in other problems.

BYPASS AND RECYCLE

Two important processing concepts are *bypass* and *recycle*. We may illustrate them with a diagram (see Fig. 3-1).

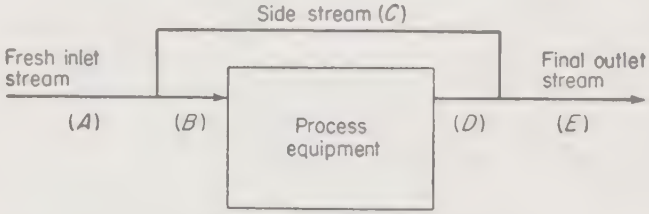


FIG. 3-1. Complex stream flow.

With bypass, part of the inlet stream is diverted around the equipment. This stream moves in parallel with the stream passing through the equipment. Streams A, B, and C are of the same composition. Streams C and D are mixed to form E. Care must be taken to distinguish between the outlet stream from the process equipment D and the final outlet stream E.

In recycle, part of the product stream is sent back to mix with the fresh feed. In this case, streams C, D, and E are of the same composition. Stream A, called the "fresh feed," and the recycle stream C are mixed to form the mixed feed B.

Bypass is sometimes used in cases where it is desired to make a relatively small change in a stream of feed. From the control standpoint, it may be much easier to make a large change in a small portion of the

feed and then to remix this with the portion of the feed which has not been processed. Such a case is illustrated in the example below.

Example 3-5. Air at 110°F, saturated with water vapor, is to be dehumidified. Part of the air is sent through a unit where it is cooled and some water condensed. This air leaves the unit saturated at 60°F. It is then remixed with the air which bypassed the unit. The final air contains 0.02 lb water vapor/lb dry air. The vapor pressure of water at 110°F is 1.2748 psia; at 60°F it is 0.2563 psia. The total pressure is 14.7 psia. Calculate the following:

a. The pounds of water vapor per pound of dry air for the original air (saturated at 110°F)

b. The pounds of water vapor per pound of dry air for the air from the dehumidifier (saturated at 60°F)

c. The ratio of pounds of dry air bypassed to pounds of dry air sent through the dehumidifier

On the basis of 10,000 ft^3 of original wet air/hr, calculate

d. The volume of wet air sent to the dehumidifier

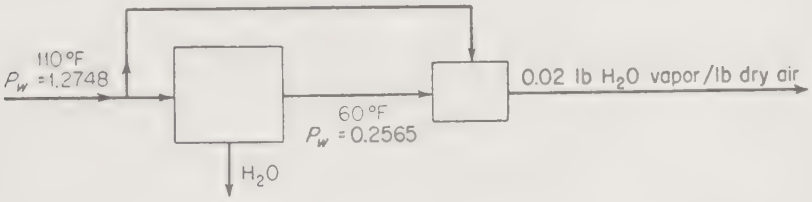
e. The volume of wet air bypassed

f. The volume of wet air leaving the dehumidifier

g. The pounds of water condensed in the dehumidifier

h. The volume of final air, assuming it is reheated to 110°F

Solution



a. lb H_2O/lb dry air for original air

$$\left(\frac{1.2748 \text{ mole } H_2O}{(14.7 - 1.2748) \text{ mole dry air}}\right)\left(\frac{18 \text{ lb } H_2O}{\text{mole } H_2O}\right)\left(\frac{\text{mole dry air}}{29 \text{ lb dry air}}\right) = \frac{0.059 \text{ lb } H_2O}{\text{lb dry air}}$$

b. lb H_2O/lb dry air for outlet air from unit

$$\left(\frac{0.2563}{14.7 - 0.2563}\right)\left(\frac{18}{29}\right) = \frac{0.011 \text{ lb } H_2O}{\text{lb dry air}}$$

c. lb dry air bypassed/lb dry air through

Basis: 1 lb dry air to dehumidifier. Let x = lb dry air in bypass stream.

Water vapor in "through" air + water vapor in bypassed air
= water vapor in final air

$$(1)(0.011) + (x)(0.059) = (1 + x)(0.02)$$
$$x = 0.231$$

d. Ft³ wet air to unit

Basis: 10,000 ft³ original air/hr

$$(10{,}000 \text{ ft}^3)\left[\frac{1}{1.231}\ (\text{fraction to unit})\right] = 8124 \text{ ft}^3$$

e. Ft³ wet air bypassed

$$10{,}000 - 8124 = 1876 \text{ ft}^3$$

f. Ft³ wet air leaving dehumidifier

$$\left[(10{,}000 \text{ ft}^3 \text{ orig air})(^{492}/_{570})\right](\text{ft}^3 \text{ at SC})\left(\frac{\text{lbmole}}{359 \text{ ft}^3}\right)$$
$$= 24.04 \text{ mole orig wet air}$$

$$(24.04 \text{ mole wet air})\left(\frac{1.2748 \text{ mole } H_2O}{14.7 \text{ mole wet air}}\right)$$
$$= 2.085 \text{ mole } H_2O \text{ in orig wet air}$$
$$24.04 - 2.085 = 21.95 \text{ mole total dry air}$$

$$(21.95)\left(\frac{1 \text{ mole dry air to unit}}{1.231 \text{ mole total dry air}}\right) = 17.84 \text{ mole dry air to unit}$$

$$(17.84 \text{ mole dry air})\left(\frac{0.2563 \text{ mole } H_2O}{(14.7 - 0.2563) \text{ mole dry air}}\right)$$
$$= 0.3165 \text{ mole } H_2O \text{ leaving unit}$$

Therefore $17.84 + 0.3165 = 18.16$ mole wet air leaving unit

and $$[(18.16)(359)](^{520}/_{492}) = 6890 \text{ ft}^3$$

g. lb H_2O condensed

$$(2.085 \text{ total mole } H_2O \text{ vapor})\left(\frac{1}{1.231}\right) = 1.694 \text{ mole } H_2O \text{ to unit}$$
$$1.694 - 0.317 = 1.377 \text{ mole } H_2O \text{ condensed}$$
$$(1.377)(18) = 24.8 \text{ lb } H_2O \text{ condensed}$$

h. Ft³ final air

24.04 total mole air − 1.38 mole H_2O condensed
= 22.66 mole final mixture

$$[(22.66)(359)](^{570}/_{492}) = 9425 \text{ ft}^3$$

Recycle. The recycle principle may be used for many different reasons. For example,

The unreacted materials leaving an industrial reactor are usually separated from the effluent stream and returned.

The top vapor from a distillation column is condensed, and usually part of it is returned to the top of the column. This particular recycle is called *reflux*.

One method of controlling temperature at a particular point in a process is to recycle part of the stream through a heat exchanger.

In a drying operation, part of the humid air may be recycled and mixed with fresh feed air. This is usually done to reduce the rate of drying when the material being dried must dry slowly. Try the following example.

Example 3-6. A solid material with 15 %w H_2O is dried to 7 %w H_2O under the following conditions: Fresh air is mixed with recycled air and is blown over the solid. The fresh air contains 0.01 lb H_2O/lb dry air and the recycled air, which is part of the air leaving the drier, contains 0.1 lb H_2O/lb dry air. The proportions of fresh and recycled air are adjusted so that the mixture entering the drier contains 0.03 lb H_2O/lb dry air.

a. How many pounds of water are removed from 100 lb of wet material fed to the drier?

b. How many pounds of dry air are in the fresh-air feed per 100 lb of wet material?

c. How many pounds of dry air are recycled per 100 lb of wet material?

d. Draw a diagram of the process, indicating the amounts of materials in each stream per 100 lb of wet material.

Solution

Basis: 100 lb wet material processed

a. lb H_2O removed. Let x = lb final material.

$$(100 \text{ lb orig material}) \left(\frac{85 \text{ lb dry solid}}{100 \text{ lb orig material}} \right) = (x \text{ lb final material}) \left(\frac{93 \text{ lb dry solid}}{100 \text{ lb final material}} \right)$$

$$x = 91.40 \text{ lb}$$

Therefore, $100 - 91.40 = 8.60$ lb H_2O removed

b. lb dry air in fresh-air feed. The amount recycled does not enter into this calculation. The pounds of dry-air feed equals the pounds of dry air leaving.

$$\frac{0.10 \text{ lb } H_2O}{\text{lb dry air leaving}} - \frac{0.01 \text{ lb } H_2O}{\text{lb fresh dry air}} = \frac{0.09 \text{ lb } H_2O \text{ removed}}{\text{lb fresh dry air}}$$

and $$(8.60 \text{ lb } H_2O) \left(\frac{\text{lb dry air}}{0.09 \text{ lb } H_2O} \right) = 95.6 \text{ lb fresh dry air}$$

c. lb recycled dry air. Let x = lb recycled dry air/lb fresh dry air.

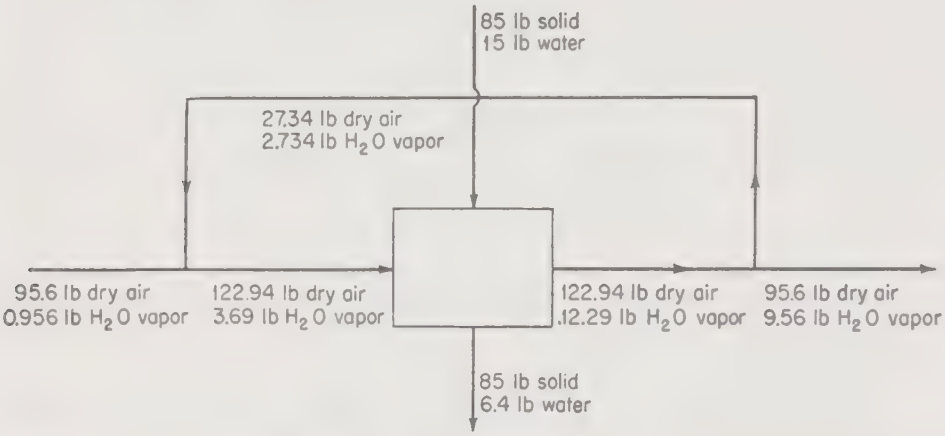
$$\frac{0.01 \text{ lb } H_2O}{\text{lb fresh dry air}} + \left(\frac{0.1 \text{ lb } H_2O}{\text{lb recycled dry air}}\right)\left(\frac{x \text{ lb recycled dry air}}{\text{lb fresh dry air}}\right) = \left(\frac{0.03 \text{ lb } H_2O}{\text{lb mixed dry air}}\right)\left[\frac{(1 + x) \text{ lb mixed dry air}}{\text{lb fresh dry air}}\right]$$

$$x = 0.286$$

and

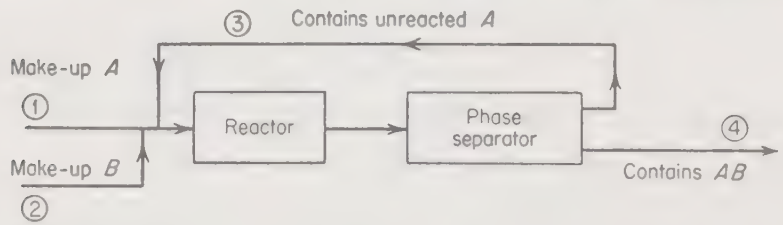
$$(95.6 \text{ lb fresh dry air})(0.286) = 27.34 \text{ lb recycled dry air}$$

d. Diagram



Recycle in connection with a reactor is much more challenging than the type shown above. The progressive examples below give an indication of the complications that may be encountered.

Example 3-7. Two pure organic chemicals A and B are introduced



into the apparatus shown in the figure for the purpose of making the compound AB. Stream flows are adjusted so that the mole ratio of A to B in the reactor is 4:1. At the temperature and pressure employed, this mole ratio effects complete consumption of B. Ninety per cent of the B forms AB, the desired product. The remainder forms A_2B, a useless by-product. A_2B is incapable of further reaction. The effluent stream from the reactor is cooled to 20°C, at which temperature A and AB are completely immiscible. A_2B, however, is soluble in A and in AB. The

distribution coefficient is

$$K = \frac{C_{AB}}{C_A} = 6$$

where C_{AB} = mole A_2B/mole AB and C_A = mole A_2B/mole A.

Calculate the amount of all materials flowing in each numbered stream, per 100 mole of desired product AB in stream 4.

Solution

Basis: 100 mole B reacted

$$A + B \rightarrow AB$$

Ninety mole B reacts with 90 mole A to give 90 mole AB.

$$2A + B \rightarrow A_2B$$

Ten mole B reacts with 20 mole A to give 10 mole A_2B.

$$90 + 20 = 110 \text{ mole } A \text{ reacts}$$

Basis: 100 mole AB produced

Stream 1:

$$\left(\frac{110 \text{ mole } A}{90 \text{ mole } AB}\right)(100 \text{ mole } AB) = 122 \text{ mole } A$$

Stream 2:

$$\left(\frac{100 \text{ mole } B}{90 \text{ mole } AB}\right)(100 \text{ mole } AB) = 111 \text{ mole } B$$

The only place that A_2B can leave the process is with AB. After start-up, the recycle stream will constantly change composition until the steady state has been reached. Under steady-state conditions 10 mole A_2B must leave with every 90 mole AB, or

Stream 4:

$$\left(\frac{10 \text{ mole } A_2B}{90 \text{ mole } AB}\right)(100 \text{ mole } AB) = 11 \text{ mole } A_2B$$

The concentration of stream 3 is that in equilibrium with stream 4, and

$$\frac{C_{AB}}{C_A} = \frac{11/100}{C_A} = 6$$

$$C_A = \frac{11 \text{ mole } A_2B}{600 \text{ mole } A}$$

The amount of A is determined by the 4:1 mole ratio requirement. Since 122 mole A is supplied per 111 mole B, 444 − 122 = 322 mole of A must be in the recycle stream.

Stream 3:

322 mole A and $(11/600)(322)$ = 5.88 mole A_2B per 100 mole AB in stream 4

Example 3-8. Suppose that the system in Example 3-7 is complicated by the fact that AB is soluble to some extent in A. If the AB is allowed to recycle, it will react with A to form A_2B. Suppose further that we believe that the cost of recovering AB from stream 3 would be prohibitive, and we desire to calculate stream compositions if dissolved AB is allowed to recycle. The solubility of AB in A is 2 mole/100 mole A and is unaffected by the presence of A_2B. The distribution coefficient of A_2B is unaffected by the presence of dissolved AB in the A phase, and $C_{AB}/C_A = 6$ when the concentrations are defined *exactly as before*. Assume that all AB entering the reactor is converted to A_2B, and calculate stream flows per 100 mole of AB in stream 4.

Solution

Basis: 100 mole A in the recycle stream. Let x = mole A in stream 1. Since the ratio of A to B entering the reactor is 4:1,

$$\frac{100 + x}{4} = \text{mole } B \text{ in stream 2}$$

There is 2 mole AB entering the reactor, and this forms 2 mole A_2B.

$$\left(\frac{100 + x}{4}\right)(0.9) = \text{mole } AB \text{ formed from } B$$

and

$$\left(\frac{100 + x}{4}\right)(0.1) = \text{mole } A_2B \text{ formed from } B$$

$(0.9)[(100 + x)/4]$ mole A was consumed to form AB from B and $(0.1)[(100 + x)/4]$ 2 mole A was consumed to form A_2B from B. In addition, 2 mole A reacted with the 2 mole of AB in the recycle stream. Since no A leaves in stream 4, all of the "make-up" A in stream 1 must be consumed. Therefore,

$$x = 2 + (0.9)\left(\frac{100 + x}{4}\right) + (0.2)\left(\frac{100 + x}{4}\right)$$

Solving,

$$x = 40.7 \text{ mole } A \text{ in stream 1}$$

$$\frac{140.7}{4} = 35.2 \text{ mole } B \text{ in stream 2}$$

The only AB leaving the reactor is that made from entering B, and $(0.9)(35.2) = 31.68$ mole AB enters the phase separator. Therefore 29.68 mole AB leaves in stream 4, and 2 mole AB recycles.

The A_2B will build up in the recycle stream until the amount leaving in stream 4 equals the amount formed in the reactor.

$$(35.2 \text{ mole } B)\left(\frac{0.1 \text{ mole } A_2B \text{ formed}}{\text{mole } B}\right) = 3.52 \text{ mole } A_2B$$

3.52 + 2 mole A_2B made from AB = 5.52 mole A_2B made in the

reactor and leaving in stream 4. The concentration of A_2B in stream 4 is 5.52 mole A_2B/29.68 mole AB. The concentration of A_2B in stream 3 is one-sixth of this and

$$\left(\frac{5.52 \text{ mole } A_2B}{(6)(29.68) \text{ mole } A}\right)(100 \text{ mole } A) = 3.09 \text{ mole } A_2B \text{ in stream 3}$$

All the above values are on the basis of 100 mole A in the recycle stream. This corresponds to 29.68 mole AB in the product stream. All the answers must be multiplied by 100/29.68, or 3.37, to put them on the required basis of 100 mole AB produced.

Stream 1:	(40.7)(3.37)	= 137.2 mole A
Stream 2:	(35.2)(3.37)	= 118.6 mole B
Stream 3:	(100)(3.37)	= 337 mole A
	(2)(3.37)	= 6.74 mole AB
	(3.09)(3.37)	= 10.40 mole A_2B
Stream 4:	(29.68)(3.37)	= 100 mole AB
	(5.52)(3.37)	= 18.60 mole A_2B

As a check, 100 + 18.60 = 118.6 mole B leaves in stream 4, and 118.6 mole B enters in stream 1.

100 + (2)(18.6) = 137.2 mole A leaves in stream 4, and 137.2 mole A enters in stream 1.

Also,	337 + 137.2 = 474
and	(4)(118.6) = 474

so that the ratio of $A:B$ entering the reactor is 4:1.

Now add the complications that B does not react completely and must be later removed from AB and recycled, that the reaction forms other products which distribute between the layers and react when they are repassed through the reactor, and that the distribution coefficients and solubilities are affected by the presence of other compounds, and you begin to appreciate a real industrial problem. In most cases a phase separation cannot be used, and the reactor effluent must be passed through a chain of processing equipment. In that event, the recycle streams originate at one or more points farther downstream from the reactor.

PROBLEMS

3-1. Pure oxygen is mixed with air to produce an "enriched air" containing 50%m O_2. What ratio of oxygen to air should be used?

3-2. A mixture of NaOH, NaCl, and $MgCl_2$ contains 34.6%w chloride and 20.0%w hydroxide, i.e., 34.6% Cl and 20.0% OH. What are the weight and mole fractions of NaOH, NaCl, and $MgCl_2$ in the mixture?

3-3. Water is being pumped under pressure to a process. It is desired to add a salt to this water in order that the solution fed to the process be exactly 4%w salt. Because of the difficulty of metering a solid into a fluid stream under pressure, the following procedure is to be used: Part of the entering water is bypassed through a large container of the solid salt, where it becomes saturated. This saturated stream is mixed with the pure water to form the 4% solution. If the saturated solution is 17%w, what percentage of the water stream must be bypassed through the saturator? If two identical rate meters are used, one in the portion of the water which is not bypassed and one in the stream which is bypassed, what must be the ratio of the reading on one meter to that on the other?

3-4. Two process streams are mixed to form a single stream. Only the flow in the mixed stream is known. A soluble salt is added to one of the original streams at a steady rate. Samples taken of this stream show it to be 4.76%w salt. Samples from the combined stream show 0.62%w salt. What is the ratio of the flows in the two original streams?

3-5. Calculate the weight rate of flow in lb/hr of NH_3 through a pipe from the following data: A stream of pure oxygen is admitted to the NH_3 line at a rate of 40 ft^3/min, and the resulting mixture is sampled farther along the pipe and found to contain 10%v O_2. The entering oxygen is metered at 18 psia and 85°F.

3-6. A mixed acid containing 65%w H_2SO_4, 20% HNO_3, and 15% H_2O is to be made by blending the following liquids:

a. A spent acid containing 10% HNO_3, 60% H_2SO_4, and 30% H_2O

b. A concentrated nitric acid containing 90% HNO_3 and 10% H_2O

c. Concentrated sulfuric acid containing 95% H_2SO_4 and 5% H_2O

How many pounds of each of the three must be used to obtain 1000 lb of mixed acid?

3-7. A mixed acid containing 65%w H_2SO_4, 20% HNO_3, and 15% H_2O is to be made by blending the following liquids:

a. A spent acid containing 10% HNO_3, 60% H_2SO_4, and 30% H_2O

b. A concentrated nitric acid containing 90% HNO_3 and 10% H_2O

c. 20% oleum (80% H_2SO_4 and 20% SO_3)

How many pounds of each of the three acids must be used to obtain 1000 lb of mixed acid?

3-8. The waste acid from a nitration operation contains 23%w HNO_3, 57% H_2SO_4, and 20% H_2O. It is specified that the concentrated acid product should contain 27% HNO_3, 60% H_2SO_4, and 13% H_2O. If the H_2SO_4 available contains 7% H_2O and the HNO_3 contains 10% H_2O, how many pounds of each must be added to produce 1000 lb of product?

3-9. Two engineers are calculating the average molecular weight of a gas mixture containing oxygen and other gases. One of them, using the correct molecular weight of 32 for oxygen, determines the average molecular weight correctly as 39.2. The other, using an incorrect value of 16, determines the average molecular weight as 32.8. This is the only error in his calculations. What is the percentage of oxygen in the mixture expressed as %m?

3-10. A mixture of phenol and water, under certain conditions of temperature and composition, forms two separate liquid phases, one rich in phenol and the other rich in water. At 30°C the compositions of the upper and lower layers are 70 and 9%w phenol, respectively. If 40 lb of phenol and 60 lb of water are mixed and the layers allowed to separate at 30°C, what will be the weights of the two layers?

3-11. Dry nitrogen is bubbled through benzene at 800 mm Hg and 50°C at a rate of 10 $in.^3$/min. The nitrogen, saturated with benzene vapor, leaves at 740 mm Hg and 40°C at a rate of 13.85 $in.^3$/min.

a. From these data, calculate the vapor pressure of benzene at 40°C, the exit temperature.

b. Derive an equation giving the lb benzene/lb dry N_2 in terms of the partial pressure of benzene, the total pressure, and the molecular weights.

c. Show the form of the equation when mole fractions are substituted for pressures.

d. Calculate the lb benzene/lb dry N_2 for this example.

3-12. A stream of gas at 70°F and 14.3 psia and 50% saturated with water vapor is passed through a drying tower where 90% of the water vapor is removed. Calculate the pounds of water removed per 1000 ft^3 of entering gas. The vapor pressure of water at 70°F is 0.74 in. Hg, and 1 atm ≈ 14.7 psi ≈ 29.92 in. Hg.

3-13. A gas mixture is known to consist of CO_2, N_2, and H_2O. It is analyzed by first passing it through a drying train where all the water is removed. The remaining gases are placed in a 1-liter flask and weighed. In one analysis 0.0843 g of water is removed in the train. The remaining gases weigh 1.5550 g at 30°C and 1 atm. What are the composition (%m) and the Orsat analysis of the original gas mixture?

3-14. In testing filter media for a proposed installation, a laboratory technician suspends 50 g of a slightly soluble salt in 100 g of water. By filtration, he obtains a wet filter cake (precipitate) weighing 53.9 g and a clear filtrate solution. He dries the cake and finds that it weighs 49.0485 g. Calculate the solubility of the salt in g/100 g of water. The concentration of the salt in the filtrate is the same as that in the liquid which adheres to the solid precipitate.

3-15. One ton of a 30%w solution of Na_2CO_3 in water is cooled slowly to 20°C. During the cooling, 10% of the water originally present is evaporated. The carbonate precipitating out forms crystals of $Na_2CO_3 \cdot 10H_2O$. If the solubility of anhydrous Na_2CO_3 at 20°C is 21.5 lb/100 lb H_2O, what weight of $Na_2CO_3 \cdot 10H_2O$ crystallizes out?

3-16. One hundred grams of a mixture of $Na_2SO_4 \cdot 10H_2O$ and $Na_2CO_3 \cdot 10H_2O$ is heated to drive off the water of hydration. The final weight of the mixed salts is 39.6 g. What is the ratio of moles of Na_2CO_3 to moles of Na_2SO_4 in the original hydrated salts?

3-17. Two salts, *A* and *B*, are dissolved in water. At the temperature of the experiment, the solubility of *A* is 1 lb *A*/lb pure water, and that of *B* is 0.4 lb *B*/lb pure water. It may be assumed that the solubilities of the two salts are not affected by the presence of each other; i.e., 1 lb water will dissolve 1 lb *A* plus 0.4 lb *B*. When water is evaporated, the concentration of the solution increases. However, if the concentration reaches the saturation point for either salt, then further evaporation will cause crystallization of that salt, while the concentration of that salt in the solution remains constant at the saturation point.

If, originally, 20 lb *A* and 20 lb *B* are dissolved in 100 lb of water, and some of the water is then evaporated from the solution, calculate (1) the amount evaporated, (2) weight of the final solution, (3) composition of the solution, and (4) the amount of each salt crystallized out, for the following cases:

a. Fifty per cent of the water originally present is evaporated.

b. Enough water is evaporated to reduce the total weight of solution and crystals to 50% of the initial value.

c. Enough water is evaporated to leave the solution saturated with *A*, without crystallizing any *A*.

d. Enough water is evaporated so that the remaining solution (not including crystals) is 50% of the original value.

3-18. Limestone is a mixture of calcium and magnesium carbonates and inert material. Lime is made by calcining the carbonates, i.e., heating them until CO_2 is

driven off by the reactions

$$CaCO_3 \rightarrow CaO + CO_2$$

and

$$MgCO_3 \rightarrow MgO + CO_2$$

When a pure limestone, consisting of the carbonates only without inert material, is calcined, 44.8 lb of CO_2 is obtained per 100 lb of limestone. What is the composition of the limestone?

3-19. In an experiment, pure carbon is burned with an enriched air consisting of 50%m O_2 and 50% N_2. Because of faulty combustion, not all the carbon burns. Of that which does burn, three times as much goes to form CO as that which goes to CO_2. The excess of oxygen is 10%. It is known that 51.3 liters of combustion gases, measured at 27°C and 1 atm, are formed for 10 g of carbon supplied (not all burned). What percentage of the carbon is unburned?

3-20. Pure sulfur is burned with air (21%m O_2 and 79% N_2). If 20% excess oxygen is used, above that necessary for complete combustion of the sulfur to SO_3, but only 30% of the sulfur burns to SO_3, the remainder going to SO_2,

a. What is the analysis (%m) of the resulting mixture of gases?

b. The gases from initial burning are passed through a converter where a conversion of SO_2 to SO_3 takes place. No new material is added here. If the gases leaving the converter have a mole fraction of oxygen of 0.043, what is the ratio of moles of SO_3 to moles of SO_2 in the converter gases?

3-21. An organic liquid of specific gravity 0.8, relative to water at 4°C, is vaporized and mixed with air. Some of the mixture is trapped over water at 20°C. After saturation with water vapor, the volume is 1000 cm^3 at 20°C and a total presssure of 730 mm Hg. A volumetric analysis shows the gas is 6.83% O_2. The specific gravity of the sample (including water vapor) is 1.642, relative to air at the same temperature and pressure. What volume of the liquid compound must be vaporized to make up this sample?

3-22. Ammonia is made by the reaction of nitrogen and hydrogen under high pressure and temperature. In order to prepare feed gas for the reactor, pure hydrogen is mixed with air (21% O_2, 78% N_2, 1% A) and the oxygen removed by water formation. The resulting mixture, after compression and drying, is to have the proper stoichiometric ratio of H_2/N_2 for NH_3 formation. On a basis of 100 mole of air, how many pounds of water would condense from the mixture of H_2, N_2, H_2O, and A when the gases are cooled from the combustion temperature to 70°F and 2 atm pressure?

3-23. At 400°C and 10 atm it is found that, for the ammonia reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

the partial pressures of the three gases are related by the expression

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$$

K_p is called an *equilibrium constant.*

When 1 mole of N_2 and 3 mole of H_2 are heated to 400°C and allowed to come to equilibrium at 10 atm, 0.148 mole of NH_3 is formed.

a. How many moles of nitrogen have been consumed? How many are unconsumed?

b. How many moles of hydrogen have been consumed? How many are unconsumed?

c. What are the partial pressures of nitrogen, hydrogen, and ammonia in the equilibrium mixture?

d. What is the value of K_p? What are its units?

e. If 2 mole of N_2 and 3 mole of H_2 are heated to 400°C and allowed to reach equilibrium at 10 atm, how many moles of NH_3 are formed?

f. What is the percentage conversion of the limiting reactant under these conditions?

3-24. A drier with a capacity of 800 lb per 24-hr day operates on a material which is 90% w H_2O and 10% solids. The product which contains 20% H_2O is dried in another oven until the water content reaches 2%. Calculate the percentage of the original water that is removed in each oven, and the weight of product per day from each of the two driers.

3-25. Ethylene oxide, C_2H_4O, may be made by passing ethylene, C_2H_4, and air over a catalyst at 250°C. When the resulting mixture is cooled and passed through water, the ethylene oxide combines with water to form ethylene glycol $(CH_2OH)_2$. In one experiment a 5%v ethylene–95%v air mixture is passed over the catalyst. Some of the ethylene does not react, some forms ethylene oxide, and some is oxidized completely to form CO_2 and water vapor. The entire gas mixture enters directly into an absorption system where it is contacted by water. The gases leaving the absorber contain all the N_2, unreacted C_2H_4, unused O_2, and the CO_2 formed. They are saturated with water vapor at a partial pressure of 15.4 mm Hg. The total pressure is 730 mm Hg. An Orsat analysis of the gases leaving the absorber shows 1.075% C_2H_4, 80.7% N_2, and 4.30% CO_2. One mole of liquid water is fed to the absorber per 100 mole of gas fed to the catalyst chamber. What is the composition (%m) of the ethylene glycol–water product formed?

3-26. The gases entering an NH_3 reactor are in a mole ratio of 4 H_2:1 N_2. The mole ratio of these gases in the exit stream is 4.25. What volume of entering gas, measured at 500°C and 1 atm, must enter the reactor to produce 150 tons of NH_3 per day?

3-27. When pure carbon is burned in air, some of it oxidizes to CO_2 and some to CO. If the ratio of N_2:O_2 = 7.18, and the ratio of CO:CO_2 = 2, what is the per cent excess air used? The exit gases contain only N_2, O_2, CO, and CO_2.

3-28. Three gaseous mixtures, with the following compositions in %m, are to be

Gas	I	II	III
CH_4	25	35	55
C_2H_6	35	20	40
C_3H_8	40	45	5

blended in such proportions that the final mixture contains 40% CH_4, 35% C_2H_6, and 25% C_3H_8. In what proportions should they be mixed?

3-29. Three gaseous mixtures, with the following compositions in %m, are blended

Gas	I	II	III
CH_4	25	25	60
C_2H_6	35	30	25
C_3H_8	40	45	15

into a single mixture. A new analyst reports that the composition of the mixture is 25% CH_4, 25% C_2H_6, and 50% C_3H_8. Without making any detailed calculations, explain how you know the analysis is incorrect.

3-30. The gases entering an ammonia reactor analyze 20%m N_2, 75% H_2, and 5% inerts. Only the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

takes place. The ratio of hydrogen to nitrogen in the outlet gases is reported as 2.85. Without detailed calculations, explain why you know this figure is incorrect.

3-31. In many cases of low solubility, a direct proportionality exists between the mole fraction of a dissolved gas in a solvent and the partial pressure of the gas in the gas phase:

$$x = Kp$$

When p is expressed in millimeters of mercury, the solubilities of oxygen and nitrogen in water at 20°C are given by the equation above, where $K_{O_2} = 0.033 \times 10^{-6}$ and $K_{N_2} = 0.0165 \times 10^{-6}$. If 1 gmole of dry air at 20°C and 5 atm total pressure is placed in contact with 10 gmole of water at 20°C and allowed to come to equilibrium at this temperature,

a. How many grammoles of oxygen dissolve?

b. How many grammoles of nitrogen dissolve?

c. How many grammoles of water vaporize, assuming water exerts its vapor pressure?

d. What are the absolute and relative volume changes in the gas phase?

3-32. In certain composition ranges ethylene tetrachloride (C_2Cl_4), water, and isopropyl alcohol ($CH_3CHOHCH_3$) separate into two liquid phases. Approximate equilibrium data are given in the table. Calculate the relative amounts and compositions of the two phases for an over-all composition of 40%w C_2Cl_4, 40% $CH_3CHOHCH_3$, and 20% H_2O

Lower layer, %w			Upper layer, %w		
C_2Cl_4	$CH_3CHOHCH_3$	H_2O	C_2Cl_4	$CH_3CHOHCH_3$	H_2O
100	0	0	0	0	100
94	5	1	1	33	66
88	10	2	21	49	30
82	15	3	35	46	19
76	20	4	50	38	12

Chapter 4

ENERGY BALANCES

In addition to being concerned with the quantities of material being processed in an industrial operation, chemical engineers are concerned with the quantities of energy being released and absorbed. The science which deals with energy and its transformations is called *thermodynamics*. This word suggests heat (thermo) and motion (dynamics). It is not entirely correct in its connotations. We shall see that we are interested in work and energy as well as in heat.

The structure of thermodynamics rests upon a few fundamental principles. The laws are derived from experimental and theoretical observations of energy, work, and heat, as correlated with such measurable properties as pressure, volume, temperature, and composition. It was once thought that heat (called "caloric") was a substance. Since it went upward when released, as in a flame, it was even assigned a negative weight. This theory was not easily discarded. Its validity was questioned in 1798 by Count Rumford, who made measurements on the rise in temperature and amounts of metal rubbed off in the boring of cannon. Later experiments of Joule in about 1840 contributed to the establishment of the law of conservation of energy as we now know it. His work with systems which underwent no net change demonstrated that the ratio of the amount of heat produced in a process to the amount of work done was constant. At this time it had been demonstrated by physicists that energy was conserved in purely mechanical systems (as, for example, the conversion of energy stored in a rotating flywheel to potential energy of a raised weight). The experiments of Joule and others led to the inclusion of other forms of energy in the law of conservation of energy and eventually to the conclusion that heat was not a substance of negative weight.

As the work on energy transformations progressed, it appeared that there were limitations on the direction a process would take or how far a process might go toward completion. The development of a limiting law started with the theoretical work of Carnot in 1824 concerning the conversion of heat to work in a heat engine. Further developments by Kelvin and Clausius brought this limiting law closer to its present-day

status. A layman's statement of the "limiting" law might be that "water will not flow uphill." But, more generally, if a process has a tendency to occur, this tendency is in one direction (downhill) only. In order to reverse a spontaneous process, it is necessary to employ an external energy source.

In spite of the development of thermodynamic laws by some of the outstanding scientists and philosophers of the past, the acceptance of these ideas in applied science was not at all rapid. Present-day usage in chemistry and chemical engineering is due largely to the effort of J. Willard Gibbs of Yale University. All of the basic research which had been done led to a variety of systems of measurement, expression of laws, nomenclature, and mathematical functions. It was not an easy matter to take these seemingly unrelated pieces of work and do something "practical" with them. Gibbs made it possible to use thermodynamics in our work by settling many of the differences and extending the concepts to things we commonly measure in the laboratory and plant.

In recent years another principle has been developed. It deals with energy contents and other properties of materials at absolute zero of temperature. Its application leads to the determination of many properties, such as the energy of a substance, on an absolute basis.

Most principles, or laws, of science are named after the originator. Thus we have Newton's laws of motion, Einstein's theory of relativity, the Pythagorean theorem, etc. The laws of thermodynamics, however, are merely numbered, perhaps because so many people have contributed to their formulation. The numbering of the laws does not even follow their chronological development, the second law having been formulated before the first.

The law of conservation of energy is called the *first law*. Its application allows calculations of energy relationships associated with all kinds of processes.

The limiting law is called the *second law*. Useful limiting-law relationships depend upon equations and functions which are derived from basic second-law considerations. By proper application of these principles we are able to calculate such things as the maximum power output from a power plant and equilibrium yields in chemical reactions.

The law dealing with properties at absolute zero is called the third law. In most cases, it is possible from the first and second laws to calculate only *relative* quantities or *changes in properties* during a process. Proper application of the third law enables us to calculate absolute rather than relative quantities. The direct use of the third law is rarely necessary in engineering work.

From the standpoint of the applications in this course, only the first

law need be considered. Further treatment of thermodynamics is therefore restricted to this law.

THE FIRST LAW

In Chap. 3 the law of conservation of matter was expressed by the statement that matter is conserved in any ordinary chemical or physical process. The word "ordinary" was included in the statement to exclude nuclear reactions, which require more advanced and special treatment. The first law of thermodynamics, also known as the law of conservation of energy, is expressed by an equally simple and parallel statement: *In any ordinary chemical or physical process, energy is neither created nor destroyed.*

Unlike the law of conservation of matter the first law of thermodynamics deals with quantities which are difficult to describe. The physicist may find himself asking just what matter is, but the engineer is generally satisfied that he understands matter sufficiently well to handle it, both in his calculations on paper and in its physical reality in the plant. The first law, however, deals with energy, which takes many diverse forms. Thus it is necessary at this point to define several concepts before proceeding with the mathematical statements of the first law which will be used in numerical calculations.

Before any equations can be written or any numerical values assigned, it is necessary to know to what these equations and numbers refer. A *system* is any portion of the universe which is set aside for study. The system chosen will depend, of course, upon the particular problem to be solved and the data available. Once a system has been chosen, the rest of the universe is called the *surroundings*. (The use of the word "universe" is common in thermodynamic terminology. It is interpreted to mean that the surroundings should be so large that any energy effects to be studied will be confined to the system and the surroundings.)

A system is described by specifying that it is in a certain *state*. This is another way of saying that it has certain properties. Just as a point may be located by mathematical coordinates, so the state of a system is described by thermodynamic coordinates (numerical values of measurable and derived quantities). Depending on the nature of the system—its number of phases and chemical species—a certain number of properties must be known in order to specify the state. In general, for a given amount of material the state is fixed by a relatively few quantities, say the temperature, pressure, and composition.

The state of a system is reproducible. Thus, the density of a gas of specified composition will always be the same when this gas is subjected to the same temperature and pressure. Other properties, such as internal

energy, will also be entirely fixed when a definite state is attained.

A system in one state may be changed to another state by varying the properties. The *path*, or series of values the variables assume in passing from one state to another, defines a *process*. In general, the choice of a path for a particular process is a choice among an infinite number of possibilities. From the laboratory and industrial standpoints, certain processes are more common than others; important ones are *isothermal*, *isobaric*, and *isochoric*, meaning constant temperature, pressure, and volume, respectively, and *adiabatic*. This latter term is described in detail later in the chapter.

Since the first law of thermodynamics deals with *energy*, we must have a clear definition of this term. The amount of energy possessed by a system is a measure of its ability to do *work*. This leads to the necessity of establishing a definition of the term *work*. Mathematically, work is the product of a force times an amplitude factor. It is best shown in differential-equation form, such as

$$dW = F\,ds \tag{4-1}$$

where W = work
F = force
s = distance

Any convenient units may be used. A common unit for work in the English engineering system is the foot-pound, abbreviated ft-lb, where pound refers to a pound force.

An excellent treatment of different types of systems may be found in the text "Heat and Thermodynamics"* by Zemansky. The equations for work in all these are shown to be analogous. For example, in stretching a wire,

$$dW = -\tau\,dL$$

where τ = tension and L = length. (The minus sign is used to obtain consistency in the definition of work, as described later.)

Let us investigate a system to find out what potential it possesses for doing work. Choose as an example a rigid container filled with a substance. Imagine that the container itself has no mass (is weightless) and does not possess other properties which need be considered in this discussion. In other words, we shall focus our attention on the substance within the container.

The most evident energy possessed by the system is *potential energy* (or potential mechanical energy). If the substance is situated a distance Z above some selected datum plane, for example the earth's surface, it could theoretically be connected to an equal weight by a pulley arrange-

* Mark W. Zemansky, "Heat and Thermodynamics," 4th ed., McGraw-Hill Book Company, Inc., New York, 1957.

ment (assumed frictionless). By allowing the substance to fall to the datum plane, it could at the same time raise this weight a distance Z. It would consequently do an amount of work equal to mZ, where m is the mass of the system.

Actually, the work done is

$$W = \int_0^Z mg\, dZ \tag{4-2}$$

where m = mass in lb (lb_m) and g = acceleration of gravity, ft/sec^2. In this system $W = (lb_m)(ft^2)/sec^2$.

In all practical engineering problems, g is essentially constant, and

$$W = mgZ \tag{4-3}$$

Furthermore, the units of W above are not the conventional ones to use in engineering work. It is customary to write

$$W = \frac{mgZ}{g_c} \tag{4-4}$$

where $g_c = 32.2\ (ft)(lb_m)/(sec^2)(lb_f)$. W is then in the usual units of ft-lb_f.

One further simplification is usually made in engineering work. Except for cases where extreme accuracy is required, the value of g is sufficiently close, numerically, to g_c so that

$$W = mZ \tag{4-5}$$

It must be emphasized that g is the acceleration of gravity and is a variable, whereas g_c is a conversion factor and is constant.

Another form of energy possessed by the system is *kinetic energy* (or mechanical kinetic energy). If the system *as a whole* is moving with a velocity u, relative to some stationary point, this kinetic energy is given by $mu^2/2$. If the mass is in lb_m and the velocity in ft/sec, the units of kinetic energy will be $(lb_m)(ft^2)/sec^2$. Again, to convert to the more common units of ft-lb, kinetic energy is usually expressed as $mu^2/2g_c$. (A similar equation may be written for energy of rotation.)

Both the potential and the kinetic energy are dependent on the *external* conditions of the system and its mass. Thus a given mass of one substance under given conditions of elevation and velocity would possess the same potential and kinetic energies as the same mass of any other substance under the same conditions. There are other forms of energy, however, which depend on the nature of the substance itself. Thus, it would seem logical that a charged storage battery would possess more capacity to do work than an uncharged one, although the two might be under such conditions that their mass, elevation, and velocities were the same.

It is logical to refer to energy associated with a substance itself as *internal energy*. This is energy possessed by the molecules themselves and is due to translational, rotational, and vibrational motion of the molecules and to the molecular configurations. It also includes the intrinsic energy of the nuclei. Fortunately, in thermodynamics it is not necessary to consider the behavior of individual molecules. Furthermore, as will be shown later, it is not necessary to know absolute values of internal energy, since we are almost always concerned with *changes* in energy. These changes in internal energy may be calculated from directly measurable properties.

There are other types of energy which may be possessed by the system and which are dependent on the material of the system itself. These are of less importance in engineering work and will not be treated in the equations to be presented. It is important to note that they may sometimes be of importance, however. One type of particular interest in some cases is *surface energy*. In order to prepare an emulsion from immiscible liquids, for example, it is necessary to perform a certain amount of work. Much of this work of subdividing the liquids into droplets and mixing them thoroughly appears in an increase of the surface energy of the mixture. At times other types of energy, such as *magnetic* and *electrostatic*, must also be considered.

We have now established that the system possesses three types of energy of engineering importance: potential energy, mZ; kinetic energy, $mu^2/2g_c$; and internal energy, mU. We might say, then, that at a particular instant the total energy E of the system is

$$E_1 = (m)\left(Z_1 + \frac{u_1^2}{2g_c} + U_1\right) \tag{4-6}$$

Consider now that the system has undergone some kind of change in state; its elevation, velocity, or internal energy has in some way been altered. Assume, however, that its mass has not changed. We may then write an equation for its energy in this new state:

$$E_2 = (m)\left(Z_2 + \frac{u_2^2}{2g_c} + U_2\right) \tag{4-7}$$

The system has undergone a change in energy:

$$\Delta E = E_2 - E_1 \tag{4-8}$$

How has the energy of the system changed? By the first law, energy is neither destroyed nor created during any ordinary chemical or physical process. The answer is that the energy of the surroundings has changed by an equal amount, opposite in sign, to compensate for the change in the system. When constant mass of the system is assumed, *the only way*

in which the system and surroundings may interchange energy is by work and heat. Work and heat are defined as energy in transit. They are not properties of a system and *cannot be stored in a system.*

Previously in this chapter we have defined work as a product of a force times an amplitude factor. Work may take on numerous forms. Two common forms are *expansion* and *electrical* work. Heat is energy in transit *as a result of a temperature difference.* Included in this is heat transfer by conduction, convection, and radiation.

Returning now to the system under consideration, assume that the system, between states 1 and 2, does an amount of work W and receives an amount of heat Q. (These must, of course, be expressed in the same units.) The system has undergone a change in its total energy ΔE. If it can exchange energy only by work and heat, then the first law may be expressed as

$$\Delta E = Q - W \tag{4-9}$$

This is the form in which the first law is usually first presented. This is the *static*, or *nonflow*, form. Reference to other texts in the field will show that E is often defined as internal energy. When the system as a whole undergoes no change in potential or kinetic energy (or surface, magnetic, or electrostatic energy) between states 1 and 2, then

$$\Delta E = \Delta U \tag{4-10}$$

Before continuing, it is necessary to examine critically the meanings of the terms Q and W. It was stated that W is the work *done by* the system and that Q is the heat *received by* the system. It is customary to make W and Q algebraically positive when these definitions are followed. (Thus, when a chemical reaction gives off heat, the sign of Q is negative.)

If we define $\Delta E'$ as the energy change of the surroundings, we may write, as a consequence of the first law,

$$\Delta E = -\Delta E' \tag{4-11}$$

Again, since energy can be transferred only by heat and work, we may write

$$-\Delta E' = Q' - W' \tag{4-12}$$

In this definition the signs of Q' and W' are such that Q' is again positive when heat is going *to the system*, and W' is positive when work is being *done by the system*. Note, however, that we have not said that $Q = Q'$ or that $W = W'$. Suppose that a gas is confined in a cylinder by a piston. The gas is the *system*, and the cylinder and piston are part of the *surroundings*. Assume that the piston is restrained from moving. The pressure of the gas is high enough to move the piston, however. If the restraints are removed, the gas will expand, and several possible processes

result. If the piston moves without friction and if the force applied to the piston is only infinitesimally less than the total force exerted on the piston face by the gas, then a *reversible* expansion results. (Note that the piston has to have negligible mass to be moved by an infinitesimal difference in pressure.) In such a case, the gas does *maximum work*, and the change in energy of the gas (negative) results in an equal increase in energy stored in the surroundings. In a general case, the gas may receive heat from the surroundings, and we may write the equation

$$\Delta E = Q - W = -\Delta E' = Q' - W' \tag{4-13}$$

In such a reversible case, the work done *by* the system is work done *on* the surroundings, and $W = W'$ and $Q = Q'$.

Consider another case in which the cylinder is completely insulated so that it receives no heat from the surroundings. Then $Q' = 0$. *This is the definition of an adiabatic process.* If the gas again expands reversibly, then again $W = W'$, and Q must be zero.

Now consider the case where the cylinder is insulated but the piston has mass and the movement of the piston involves some friction. Thus the gas does more work in moving the piston than actually is transferred to and stored in the surroundings as an appropriate form of energy. Since the process is adiabatic, $Q' = 0$, and

$$Q - W = -W' \tag{4-14}$$

Thus Q has the value $W - W'$. We have already defined Q as heat *added* to the system. In this case, Q does not come from the surroundings but is extracted from within the system by a conversion of work to heat. Such heat (or, in the case of an uninsulated cylinder where the process is irreversible and W exceeds W', the difference $Q - Q'$) might be called an internal-heat effect. In this case we might define W as internal work and W' as useful work, or work appearing in the surroundings.

We have now established the equation

$$\Delta E = Q - W = -\Delta E' = Q' - W' \tag{4-13}$$

where

$$\Delta E = \Delta U + \Delta\left(\frac{u^2}{2g_c}\right) + \Delta Z \tag{4-15}$$

for the static, or nonflow, system where mass is constant. Even this equation is further limited, in that internal movement (such as agitation) and magnetic and electrical energy have been neglected.

The energy balances studied in stoichiometry are generally *heat balances.* The kinetic- and potential-energy terms are almost always small in comparison with the change in internal energy when heat effects are present. Furthermore, we shall usually be interested in systems

where no work is done except that of expansion. In such a case,

$$\Delta E = \Delta U = Q - \int_{V_1}^{V_2} P\,dV \tag{4-16}$$

Two cases of special interest here are the constant volume, where

$$\Delta E = Q \tag{4-17}$$

and the constant pressure, where $\int P\,dV \approx P\,\Delta V \approx \Delta(PV)$,

and
$$\Delta E = Q - P\,\Delta V = Q - \Delta(PV) \tag{4-18}$$

The Flow System. The above treatment has been restricted to a study of the energy relationships in a static system. Such systems are common in the laboratory and in some industries. In most cases of industrial importance, however, *continuous* operation is used. An analysis of a continuous operation leads to a different form of the first law referred to as the *flow equation.*

Visualize a piece of equipment where a chemical or physical process is occurring. The materials to be processed are supplied to the equipment by conveyors of some sort. In most cases these are pipelines. Products are removed by the same means.

Assume first a *steady-state system.* This implies that the mass rate of feed equals the mass rate of removal of products. Also, at any specified point in the system, there is no variation with time in the velocity, temperature, pressure, or composition of the material. There is no accumulation or depletion of material or energy within the equipment. Assume further that the equipment itself is stationary; i.e., only the feed and products are in motion relative to the earth.

The general word statement of the first law is not changed by a change in the type of operation. If we choose a length of time such that 1 lb of material enters the equipment, we may make an analysis of the energy relationships involved. Thus we may say that each pound of material entering and each pound leaving possesses a certain amount of potential, kinetic, and internal energy (and other forms under special circumstances). Again we may write potential energy as gZ/g_c and internal energy as U. The kinetic energy is usually written as $u^2/2g_c$, although it may take other forms under special circumstances.

Consider now 1 lb of material passing a certain point in the pipeline leading to the equipment. The material behind it in the line supplies the pressure which forces this pound into the system. In doing so, the surroundings expand by an amount equal to the volume of the pound and do work equal to PV on that pound. This work is done at the expense of an equivalent amount of energy in the surroundings. We may therefore look upon this PV product as another type of energy, called simply

"PV energy," possessed by the entering material. In a similar manner, PV energy is returned to the surroundings by the pound of material leaving the system at the other end.

Since the material entering the equipment carries in a certain amount of energy, the material leaving removes a certain amount of energy, and energy is interchanged between the surroundings and system by work and heat only, we may write the general flow equation (often called the "total-energy balance") as

$$U_1 + P_1V_1 + \frac{gZ_1}{g_c} + \frac{u_1^2}{2g_c} + Q' - W' = U_2 + P_2V_2 + \frac{gZ_2}{g_c} + \frac{u_2^2}{2g_c} \quad (4\text{-}19)$$

As previously defined, Q' is the heat removed from the surroundings and is positive when it goes toward the system (in this case, the flowing fluid). W' is the work added to the surroundings. It is written as W_f' by some authors to emphasize the flow character of the equation in which it is used. It is also sometimes called "shaft work" since it is transmitted by a machine working on a shaft, such as a turbine or a pump.

The above equation is usually written for a 1-lb-mass basis. On the other hand, the static equation is often written for the entire system, whatever its mass.

The above derivations cover the two most common cases in ordinary practice: the batch and the continuous operations. It is possible, of course, to have more complex operations, and the added complexities show up in correspondingly more complex equations. Such cases are appropriately covered in more advanced treatments.

Now let us examine the nature of these two equations to see what forms are appropriate for our purposes. Consider first the "static" equation. We have already shown that, when the system as a whole does not change in elevation or velocity (which, in a practical case, means a piece of batch equipment sitting on a laboratory bench), we have two important cases:

Constant volume: $Q = \Delta U$ (4-20)

Constant pressure: $Q = \Delta U + \Delta(PV) = \Delta(U + PV)$ (4-21)

The flow equation may be written as

$$Q' - W' = \Delta(U + PV) + \Delta\left(\frac{gZ}{g_c}\right) + \Delta\left(\frac{u^2}{2g_c}\right) \quad (4\text{-}22)$$

The equation as it stands is the basis for much of the work in both fluid-flow and heat balances. Special forms are obtained, depending on which variables are important. We wish to find what form is suitable for use in heat-balance calculations but must first define some more terms.

Heat Capacity. Suppose that we wish to heat a given quantity of a material from one temperature, t_1, to another temperature, t_2. A certain

amount of heat is necessary. Suppose, instead, that we heat the material from t_1 to t_3, where the difference $t_3 - t_1$ is twice the difference $t_2 - t_1$. It would seem logical to say that twice as much heat would be required in the second case; i.e., the quantity of heat needed should be directly proportional to how much change we wish to cause in the temperature of the material. The above statement is "almost" true. If we restrict the temperature rise to a differential amount dt, we may write

$$dQ = C\,dt \tag{4-23}$$

where dQ is an infinitesimal quantity of heat and C is a proportionality constant.

The factor C is called a *heat capacity* or, in some cases, a *specific heat.* It varies with different substances. It also varies with the *type of process.* Referring to the two cases for the static equation, we note that in the constant-volume case $Q = \Delta U$, while in the constant-pressure case $Q = \Delta(U + PV)$. Certainly the differences ΔU and $\Delta(U + PV)$ between two temperatures will be different. Thus the proportionality factor C seems to depend on the path of a process. The two most commonly used values of heat capacity are those at constant volume and at constant pressure.

With this brief definition we are in a position to define terms necessary to further understanding of the first law. These terms are the *calorie* and the *British thermal unit* (*Btu*). A calorie is the amount of heat necessary to raise the temperature of one gram of water at constant atmospheric pressure from 14.5 to 15.5°C. A Btu is that quantity of heat necessary to raise the temperature of one pound of water from 63 to 64°F.

Now if we refer back to the general static form of the first law,

$$\Delta E = Q - W$$

we find that we may increase the energy of the system by adding heat or by doing work on the system. Once heat or work has been added, they no longer exist as such, and we say merely that the energy of the system has changed. Once the change has occurred, there is no way of telling by what means the change was brought about. In this sense, work and heat are equivalent.

We have, however, defined a quantity of work by means of a mechanical system and have established engineering units of ft-lb$_f$. Similarly, we have defined a quantity of heat in terms of a temperature change of a standard substance and established the English unit, the Btu. Obviously, we cannot add heat and work quantities unless they are expressed in the same units. The conversion factor between work and heat units is often called the *mechanical equivalent of heat.* Without exploring the

methods of determining this factor, we shall merely state its value:

$$1 \text{ Btu} \approx 778.26 \text{ (ft)(lb}_f\text{)}$$

You should memorize this factor; it will be used many times. In most engineering work the value 778 is satisfactory. Other conversion factors are given in Appendix A. Consider the following examples:

Example 4-1. A substance with a heat capacity of 0.5 Btu/(lb)(F°) enters a heat exchanger at a temperature of 40°F. It leaves at a temperature of 85°F. The exit pipe is 20 ft above the entrance. The inlet velocity is 10 ft/sec, and the exit velocity is 100 ft/sec. The flow is steady-state. There is no pump between the inlet and outlet.

a. How many Btu are needed to heat the material?

b. How many ft-lb are needed to elevate the material?

c. How many ft-lb are needed to increase the velocity?

d. When the above quantities are converted to Btu, what percentage change is there in the total heat needed?

Solution. In this case the total-energy balance, without the work term, is valid:

$$Q' = \Delta(U + PV) + \Delta\left(\frac{gZ}{g_c}\right) + \Delta\left(\frac{u^2}{2g_c}\right)$$

a. Basis: 1 lb_m of material. As we shall see presently, the term $\Delta(U + PV)$ represents the actual heat used to change the temperature. Then

$$\Delta(U + PV) = (C)(t_2 - t_1) = \left(\frac{0.5 \text{ Btu}}{\text{(lb)(F°)}}\right)(85 - 40)\ \text{(F°)} = 22.5 \frac{\text{Btu}}{\text{lb}}$$

b. $$\Delta\left(\frac{gZ}{g_c}\right) = \frac{20\text{(ft)(lb}_f\text{)}}{\text{lb}_m} \qquad \text{(assuming } g = g_c \text{ numerically)}$$

c. $$\Delta\left(\frac{u^2}{2g_c}\right) = \frac{100^2 - 10^2}{(2)(32.2)} = 153.5 \frac{\text{(ft)(lb}_f\text{)}}{\text{lb}_m}$$

d. $$Q' = 22.5 + \frac{20}{778} + \frac{153.5}{778} = 22.72 \frac{\text{Btu}}{\text{lb}}$$

$$\left(\frac{0.22}{22.5}\right)(100) = 1\%$$

Thus the potential and kinetic energies are only about 1% of the total heat requirement.

Example 4-2. Suppose that a weight with a heat capacity of 0.6 Btu/(lb)(F°) is dropped in a vacuum. As it falls, it loses potential energy which is converted to kinetic energy. When it hits a solid surface, all the kinetic energy is converted to heat. The temperature of the weight rises 1 F° as a result.

a. How far does the weight fall?

b. What is the velocity of the weight just before it hits?

Solution

Basis: 1 lb_m of the weight. The weight is the system. The static form of the first law is valid here. There is no work-producing device, and so we write

$$Q' = \Delta E = \Delta U + \Delta\left(\frac{gZ}{g_c}\right) + \Delta\left(\frac{u^2}{2g_c}\right)$$

Taking the end conditions as the two times the weight is at rest and assuming that all the energy is retained in the weight and that no external heat is added, we may say that

$$\Delta\left(\frac{u^2}{2g_c}\right) = 0$$

and

$$Q' = \Delta E = 0$$

Thus

$$\Delta U = -\Delta\left(\frac{gZ}{g_c}\right)$$

The result of the process is that the internal energy is increased. As shown previously, the temperature of a substance may rise because of the addition of energy, whether in the form of heat or work. Thus

$$\Delta U = C\,\Delta t = \left(\frac{0.6\ \text{Btu}}{(\text{lb})(\text{F}^\circ)}\right)(1\ \text{F}^\circ) = \frac{0.6\ \text{Btu}}{\text{lb}_m}$$

$$\left(\frac{0.6\ \text{Btu}}{\text{lb}_m}\right)\left(\frac{778(\text{ft})(\text{lb}_f)}{\text{Btu}}\right) = \frac{466.8(\text{ft})(\text{lb}_f)}{\text{lb}_m} = -\Delta Z\left(\frac{g}{g_c}\right)$$

$$= -\Delta Z \qquad \text{(numerically)}$$

a. The weight must fall 466.8 ft.

b. If we choose end conditions as the time the weight is initially at rest and the instant just before the weight strikes, we may say that the internal energy is unchanged, and thus

$$-\Delta Z = \Delta\left(\frac{u^2}{2g_c}\right) = \frac{u_2^2}{2g_c}$$

Therefore,

$$u_2 = \sqrt{(2)(32.2)(466.8)} = \frac{174\ \text{ft}}{\text{sec}}$$

These two illustrations bring out the important fact that, except in the most extreme cases, whenever heat effects are present because of physical processes and/or chemical reactions, potential and kinetic effects may be neglected. The steady-state flow equation for such cases may be written

$$Q' - W' = \Delta(U + PV) \tag{4-24}$$

In most problems where heat balances are made when no pump or similar work-producing device is present, the equation becomes

$$Q' = \Delta(U + PV) \tag{4-25}$$

You will note that in two cases, the constant-pressure batch and the steady-state flow, the grouping $U + PV$ has appeared. This is encountered so frequently that it has been given the name *enthalpy* and the symbol H. It is best to consider enthalpy as merely a convenient mathematical grouping rather than to attempt to give it physical significance.

We now have three equations which will be used in the rest of our work on heat balances. These are

Constant-volume batch:	$Q = \Delta U$	(4-20)
Constant-pressure batch:	$Q = \Delta H$	(4-21)
Steady-state flow:	$Q' = \Delta H$	(4-25)

These equations have been obtained from the basic first law of thermodynamics by a long derivation involving many assumptions. The equations may be used when the assumptions are valid; otherwise you must refer back to the original forms of the first law. It is advisable here to review again these assumptions:

1. In the original forms of the first law (both static and flow), internal, kinetic, and potential energy were considered important. Also, PV energy was included in the flow form. Surface, magnetic, electrical, and other forms of energy were neglected.

2. Values of g and g_c were considered so close numerically that their ratio was assumed to be unity.

3. In cases where heat effects exist, potential- and kinetic-energy effects were assumed negligible.

4. In the static, or batch, form of the equation, work was assumed to be zero in the constant-volume case [Eq. (4-20)] and $\Delta(PV)$ in the constant-pressure case [Eq. (4-21)]. This is equivalent to saying that no electrical or other forms of work other than expansion work are done.

5. In the flow form of the equation [Eq. (4-25)], external work, such as is transmitted by a pump or turbine, was neglected. Expansion work is included in the PV terms which are part of the enthalpy.

These equations as presented are valid for making heat balances. As you will see in a later study of fluid flow, different forms of the equations are obtained because different terms are important. Other forms of the equations will arise in a study of physics and physical chemistry, because again different terms are important. Good judgment is necessary in the selection of equations for the solution of a particular problem. The simplifications which can be made are dictated by the particular problem and by the accuracy of the data which are available for the solution.

TYPES OF HEAT EFFECTS

We have now established that the amount of heat associated with a process may be found if we know the values of certain thermodynamic functions such as enthalpy and internal energy. If we know how to evaluate these functions, we can then calculate heat quantities.

Heat may be absorbed or released in several ways. There is a certain *heat of reaction* associated with every *chemical process.* Purely *physical operations* often are accompanied by energy changes which may be caused by the addition or removal of work and/or heat.

Two distinct physical processes are the basis for concepts which we must explore further. We have already mentioned that the addition or removal of heat can cause the temperature of a substance to change. Energy added in the form of heat, which causes a change in the temperature of a substance *without a change of phase,* is called *sensible heat.* In contrast with this type of process, when dry ice is exposed to the atmosphere and heat is added, it sublimes directly to vapor without a change in temperature. Similarly, when water boils under constant pressure, it changes from liquid to vapor without a change in temperature. In such cases it is necessary to supply energy to cause these changes to occur. The energy necessary to cause a *phase change without a change in temperature* is called *latent heat.*

There is still another type of heat quantity which is of a combined physical-chemical nature. This is the *heat of mixing* or *heat of dilution.* You will recall the large rise in temperature when sodium hydroxide is dissolved in water or when sulfuric acid is diluted.

HEAT CAPACITIES

Let us now study more carefully the concept of sensible heat and the terms defined by it. We have already established a general equation

$$dQ = C\,dt \tag{4-23}$$

and used it as the basis for the definition of the basic heat quantities, the calorie and the Btu. We have also pointed out that the proportionality factor C is dependent upon the path of a process, since we know that Q is dependent on path. This dependency may be established by considering some paths of importance and comparing, for each case, two different equations for dQ/dt.

Suppose that we assume a substance is being heated at constant pressure. For an infinitesimal temperature change we may write

$$dQ = C_p\,dt \tag{4-26}$$

and

$$dQ = dH \tag{4-27}$$

where the subscript on the heat capacity C_p specifies that the path is constant pressure. Dividing both equations by dt, we obtain

$$C_p = \frac{dH}{dt} \tag{4-28}$$

This is usually written

$$C_p = \left(\frac{\partial H}{\partial t}\right)_p \tag{4-29}$$

to avoid possible ambiguity. In words, *the heat capacity at constant pressure is equal to the rate of change of the enthalpy with temperature at constant pressure.*

Now what can be said concerning the units of heat capacity? From the equation we may say that C_p has the units of Btu/F°, cal/C°, or any other units representing an amount of energy divided by a temperature change. Since it is evident that the heat capacity of a system should be directly proportional to the mass of the system, it is customary to define it on the basis of a unit quantity of material. For practical reasons, the heat capacity of a gas is usually on a *molal* basis, and C_p is Btu/(lbmole)(F°) or cal/(gmole)(C°). The heat capacity of a liquid or solid is usually on a *unit mass* basis and thus has the units Btu/(lb)(F°) or cal/(g)(C°). Heat capacities referred to this basis are often called *specific heats.*

All the equations which have been presented have been on a differential basis. This is because the heat capacity of a substance is not a constant but is a function of the temperature and, to a lesser extent, the pressure. Thus, in order to calculate a quantity of heat needed to produce a given temperature change, the equations to use are

$$Q = M \int_{t_1}^{t_2} C_p \, dt \tag{4-30}$$

where M is mass and C_p is defined on a mass basis, or

$$Q = N \int_{t_1}^{t_2} C_p \, dt \tag{4-31}$$

where N is moles and C_p is defined on a molal basis. Thus the relationship between heat capacity and temperature must be known before the integration can be performed. The question now arises as to the most practical method of determining the integral; this to some extent determines the most practical method of expressing the heat capacity as a function of temperature.

The heat capacity is actually a complex function of temperature. The fundamental relationships are still not entirely worked out. In the general case you will have available a tabulation of experimental values.

From these values numerous equations of a purely empirical nature have been developed. The most practical for engineering purposes are the *polynomial forms*, determined entirely by curve-fitting of experimental values

$$C_p = a + bt + ct^2 + dt^3 + \cdots \tag{4-32}$$

With many substances the heat capacity is assumed constant, and thus only the first term of the equation is used. This is usually the case where the temperature range to be covered is small or where the data are of limited accuracy. With many solids and liquids two terms are retained, giving a linear relationship of heat capacity to temperature. For most gases, especially over large temperature ranges, three terms are sufficient for engineering accuracy. Seldom is it necessary to use more than three terms.

You must exercise special care when using values of the constants taken from different sources. Depending on the origin of the data, the heat capacity may be expressed in metric or English units, and the temperature may be in any of the four scales in common use. You may also wish to convert an equation from one set of units to another. Some of these points are illustrated in the following problem.

Example 4-3. An approximate equation for the heat capacity of gaseous HCl is

$$C_p = 6.60 + 0.96 \times 10^{-3}T$$

where C_p = cal/(gmole)(K°) and T = temperature, °K. This equation is valid at atmospheric pressure.

a. What are the units of the constants?

$$a = \frac{\text{cal}}{(\text{gmole})(\text{K}^\circ)}$$

Also

$$bT = \frac{\text{cal}}{(\text{gmole})(\text{K}^\circ)}$$

Therefore

$$b = \frac{\text{cal}}{(\text{gmole})(\text{K}^\circ)(^\circ\text{K})}$$

(Note again our terminology in regard to the use of the degree sign. °K means a temperature; K° means a *difference* in temperature.)

b. How many calories are needed to heat 1 gmole from 100 to 200°C?

$$Q = \int_{T_1}^{T_2} C_p\,dT = (6.60)(T_2 - T_1) + \left(\frac{0.96 \times 10^{-3}}{2}\right)(T_2^2 - T_1^2)$$

Substituting $T_2 = 473$°K, $T_1 = 373$, $Q = 701$ cal/gmole.

c. Find the constants for C_p in cal/(gmole)(C°) and t in °C.

$$\frac{C_p \text{ cal}}{(\text{gmole})(\text{C°})} = \left(\frac{6.60 \text{ cal}}{(\text{gmole})(\text{K°})}\right)\left(\frac{1 \text{ K°}}{\text{C°}}\right) + \left(\frac{0.96 \times 10^{-3} \text{ cal}}{(\text{gmole})(\text{K°})(\text{°K})}\right)\left(\frac{1 \text{ K°}}{\text{C°}}\right)(t + 273)(\text{°K})$$

$$\frac{C_p \text{ cal}}{(\text{gmole})(\text{C°})} = 6.86 + 0.96 \times 10^{-3}t$$

d. Using the above equation, calculate the Btu to heat 1 lbmole from 100 to 200°F.

$$100°\text{F} = 37.8°\text{C} \qquad 200°\text{F} = 93.3°\text{C}$$

$$Q = [(6.86)(93.3 - 37.8) + (0.48 \times 10^{-3})(93.3^2 - 37.8^2)]\left(\frac{\text{cal}}{\text{gmole}}\right)\left(\frac{1 \text{ Btu}}{252 \text{ cal}}\right)\left(\frac{454 \text{ gmole}}{\text{lbmole}}\right) = \frac{692 \text{ Btu}}{\text{lbmole}}$$

[Note that the factor (1 Btu/252 cal)(454 gmole/lbmole) reduces to 1.8 (Btu/lbmole)/(cal/gmole).]

e. Find the constants for C_p in Btu/(lbmole)(C°) and t in °C.

$$\left(\frac{C_p \text{ cal}}{(\text{gmole})(\text{C°})}\right)\left(\frac{1.8 \text{ (Btu/lbmole)}}{\text{cal/gmole}}\right) = C_p \text{ in Btu/(lbmole)(C°)}$$

Therefore $$\frac{C_p \text{ Btu}}{(\text{lbmole})(\text{C°})} = 12.3 + 1.73 \times 10^{-3}t$$

(Comparing with part *d* you see that the factor 1.8 is now included in the constants instead of being used separately.)

f. Find the constants for C_p in Btu/(lbmole)(F°) and t in °C.

$$\frac{C_p \text{ Btu}}{(\text{lbmole})(\text{F°})} = \left(\frac{12.3 \text{ Btu}}{(\text{lbmole})(\text{C°})}\right)\left(\frac{1 \text{ C°}}{1.8 \text{ F°}}\right) + \left(\frac{1.73 \times 10^{-3} \text{ Btu}}{(\text{lbmole})(\text{C°})(\text{°C})}\right)\left(\frac{1 \text{ C°}}{1.8 \text{ F°}}\right)(t)$$

$$\frac{C_p \text{ Btu}}{(\text{lbmole})(\text{F°})} = 6.86 + 0.96 \times 10^{-3}t$$

(Note that the heat capacity is numerically the same in the two systems *at the same temperature.*)

g. Find the constants for C_p in Btu/(lbmole)(F°) and t in °F.

$$\frac{C_p \text{ Btu}}{(\text{lbmole})(\text{F°})} = \frac{6.86 \text{ Btu}}{(\text{lbmole})(\text{F°})} + \left(\frac{0.96 \times 10^{-3} \text{ Btu}}{(\text{lbmole})(\text{F°})(\text{°C})}\right)\left(\frac{t - 32}{1.8}\right)(\text{°C})$$

$$\frac{C_p \text{ Btu}}{(\text{lbmole})(\text{F°})} = 6.84 + 0.53 \times 10^{-3}t$$

h. Using the equation in part *g*, calculate the Btu to heat 1 lbmole from 100 to 200°F.

$$Q = (6.84)(200 - 100) + (\tfrac{1}{2})(0.53 \times 10^{-3})(200^2 - 100^2)$$

$$Q = \frac{692 \text{ Btu}}{\text{lbmole}}$$

(This answer is the same as obtained in part *d*.)

i. Find the constants for C_p in Btu/(lbmole)(R°) and T in °R.

$$\frac{C_p \text{ Btu}}{(\text{lbmole})(\text{R}^\circ)} = \left(\frac{6.84 \text{ Btu}}{(\text{lbmole})(\text{F}^\circ)}\right)\left(\frac{1 \text{ F}^\circ}{\text{R}^\circ}\right) + \left(\frac{0.53 \times 10^{-3} \text{ Btu}}{(\text{lbmole})(\text{F}^\circ)(^\circ\text{F})}\right)\left(\frac{1 \text{ F}^\circ}{\text{R}^\circ}\right)(T - 460)(^\circ\text{F})$$

$$\frac{C_p \text{ Btu}}{(\text{lbmole})(\text{R}^\circ)} = 6.60 + 0.53 \times 10^{-3}T$$

j. Find the constants for C_p in cal/(gmole)(K°) and T in °K.

$$\frac{C_p \text{ cal}}{(\text{gmole})(\text{K}^\circ)} = \left(\frac{6.60 \text{ Btu}}{(\text{lbmole})(\text{R}^\circ)}\right)\left(\frac{1.8 \text{ R}^\circ}{\text{K}^\circ}\right)\left(\frac{1 \text{ cal/gmole}}{1.8 \text{ Btu/lbmole}}\right) + \left(\frac{0.53 \times 10^{-3} \text{ Btu}}{(\text{lbmole})(\text{R}^\circ)(^\circ\text{R})}\right)\left(\frac{1.8 \text{ R}^\circ}{\text{K}^\circ}\right)(1.8T^\circ\text{R})\left(\frac{1 \text{ cal/gmole}}{1.8 \text{ Btu/lbmole}}\right)$$

$$\frac{C_p \text{ cal}}{(\text{gmole})(\text{K}^\circ)} = 6.60 + 0.96 \times 10^{-3}T$$

(This is the equation with which we started.)

k. Calculate the heat capacity at 212°F (100°C) using several of the above equations.

$$C_p = 6.60 + (0.96 \times 10^{-3})(373) = \frac{6.95 \text{ cal}}{(\text{gmole})(\text{K}^\circ)}$$

$$C_p = 6.86 + (0.96 \times 10^{-3})(100) = \frac{6.95 \text{ cal}}{(\text{gmole})(\text{C}^\circ)}$$

$$C_p = 6.84 + (0.53 \times 10^{-3})(212) = \frac{6.95 \text{ Btu}}{(\text{lbmole})(\text{F}^\circ)}$$

$$C_p = 6.60 + (0.53 \times 10^{-3})(672) = \frac{6.96 \text{ Btu}}{(\text{lbmole})(\text{R}^\circ)}$$

$$C_p = 12.3 + (1.73 \times 10^{-3})(100) = \frac{12.47 \text{ Btu}}{(\text{lbmole})(\text{C}^\circ)}$$

$$C_p = (1.8)(6.95) = \frac{12.51 \text{ Btu}}{(\text{lbmole})(\text{C}^\circ)}$$

The values are in agreement except for "rounding-off" errors.

There are numerous points to be made from a study of this example:

1. The units of the constants are important when making conversions. Particularly, simplifications are brought about by the use of the two symbols, such as °K and K°, representing temperature and difference in temperature. See part *a*.

2. An amount of heat is obtained by simple integration. For this case,

$$Q = N \int_{T_1}^{T_2} C_p \, dT = (N) \left[a(T_2 - T_1) + \frac{b}{2} (T_2^2 - T_1^2) + \cdots \right]$$

See part *b*.

3. When converting constants from one system to another, the factors 1 K° ≈ 1 C° ≈ 1.8 F° ≈ 1.8 R° are used for temperature *differences*. Direct conversions are used for temperatures, as for example:

t°C + 273 for T°K
$\frac{t°\text{F} - 32}{1.8}$ for t°C
T°R − 460 for t°F
1.8T°K for T°R

See parts *c*, *e*, *f*, *g*, *i*, and *j*.

4. The factor (1.8 Btu/lbmole)/(cal/gmole) should be memorized. It will be used extensively in heat-balance work. See parts *d* and *e*.

5. At the same temperature the point value of C_p is the same in both systems of units. See parts *f* and *k*.

6. Although the numerical values of C_p in Btu/(lbmole)(F°) and cal/(gmole)(C°) are the same at the same temperature, the constants in the equations are different. Compare the equations in parts *i* and *j*, *c* and *g*, and the values in part *k*.

7. At a given temperature the C_p in Btu/(lbmole)(C°) is 1.8 times the value in Btu/(lbmole)(F°), since 1 C° is 1.8 times as large as 1 F°. See parts *e* and *k*.

The last observation is the basis of definition of another heat unit occasionally used. This is the centigrade heat unit (Chu), sometimes called "pound centigrade unit" (Pcu), defined as 1.8 Btu. With this definition the heat capacity is numerically the same when expressed in Btu/(lbmole)(F°), cal/(gmole)(C°), or Chu/(lbmole)(C°).

As mentioned previously, it is often possible to estimate an average heat capacity for solids and liquids and to treat this as a constant over a temperature range. In such cases,

$$Q = \int_{T_1}^{T_2} C_p \, dT = \bar{C}_p (T_2 - T_1) \tag{4-33}$$

where $\bar{C}_p$ denotes the mean value.

In the case of gases, the heat capacity varies too much to choose a value from a table or plot and assume this value constant. Consider the following example:

Example 4-4. For CO_2 at atmospheric pressure,

$$(C_p)\left(\frac{\text{Btu}}{(\text{lbmole})(\text{F}^\circ)}\right) = 9.00 + 2.71 \times 10^{-3}t^\circ\text{F} - 0.256 \times 10^{-6}(t^\circ\text{F})^2$$

a. How much heat is necessary to heat 1 lbmole from 100 to 800°F?

$$Q = \int_{t_1}^{t_2} C_p\,dt = (9.00)(800 - 100) + (\tfrac{1}{2})(2.71 \times 10^{-3})(800^2 - 100^2) - (\tfrac{1}{3})(0.256 \times 10^{-6})(800^3 - 100^3) = 7080 \text{ Btu}$$

b. What error would result if the point value of heat capacity were used for an average value, using the lower, mid-point, and upper temperatures?

The equation for C_p is first solved; then $Q = C_p(t_2 - t_1)$. The following values result:

Temperature	C_p	Q	Per cent error
100	9.27	6489	−8.3
450	10.16	7112	+0.5
800	11.01	7707	8.8

c. What number, multiplied by the 700-degree temperature difference, gives the proper Q of 7080?

$$\frac{7080}{700} = \frac{10.11 \text{ Btu}}{(\text{lbmole})(\text{F}^\circ)}$$

The answer to part *c* is a numerical representation of the *mean heat capacity*, sometimes called the *integrated average heat capacity*. It is defined by

$$Q = \int_{t_1}^{t_2} C_p\,dt = \bar{C}_p(t_2 - t_1) \tag{4-33}$$

It may be looked upon as the proper value by which to multiply the change in temperature in order to obtain a correct value for Q. For the three-term polynomial form,

$$\bar{C}_p = \frac{a(t_2 - t_1) + \frac{b}{2}(t_2^2 - t_1^2) + \frac{c}{3}(t_2^3 - t_1^3)}{t_2 - t_1}$$

This reduces to

$$\bar{C}_p = a + \frac{b}{2}(t_2 + t_1) + \frac{c}{3}(t_2^2 + t_2t_1 + t_1^2) \tag{4-34}$$

For the two-term form of the polynomial equation, the mean heat capacity between two temperatures is numerically the same as the point value at the average temperature. The same relationships exist between

mean and point heat capacities, regardless of the temperature scales used.

Obviously, the mean heat capacity would be of little use if it were necessary to evaluate it first and then use it in a problem. A direct integration of the equation for heat capacity vs. temperature would be as easy. However, the mean values have already been evaluated for the most common gases.

Reference to the equation for $\bar{C}_p$ shows that it is a function of t_1 and t_2. Therefore, an infinite number of possible equations exists relating $\bar{C}_p$ to temperature. It is customary to fix one temperature, t_1, and leave t_2 as a variable. Since most thermochemical data are evaluated at 18, 20, or 25°C and most industrial data are based on 60 or 70°F, t_1 will almost always be one of these. You will note that all of these are close to "room temperature." With these facts in mind, let us consider further the problem of Example 4-4.

Example 4-5

a. Determine the constants in an equation for $\bar{C}_p$ for CO_2 at 1 atm, using a base temperature of 18°C (64.4°F).

$$\bar{C}_p = 9.00 + (\tfrac{1}{2})(2.71 \times 10^{-3})(t + 64.4) - (\tfrac{1}{3})(0.256 \times 10^{-6})(t^2 + 64.4t + 64.4^2)$$

$$\bar{C}_p = 9.09 + 1.35 \times 10^{-3}t - 0.0853 \times 10^{-6}t^2$$

b. Compare the point and average values at 64.4°F.

$$C_p = 9.00 + (2.71 \times 10^{-3})(64.4) - (0.256 \times 10^{-6})(64.4)^2 = 9.17$$

$$\bar{C}_p = 9.09 + (1.35 \times 10^{-3})(64.4) - (0.0853 \times 10^{-6})(64.4)^2 = 9.17$$

c. Calculate the amount of heat necessary to heat 1 lbmole from 100 to 800°F.

Q = heat to heat from 64.4 to 800°F − heat to heat from 64.4 to 100°F

$$Q = (\bar{C}_{p(800°)})(800 - 64.4) - (\bar{C}_{p(100°)})(100 - 64.4)$$

$$= (10.12)(735.6) - (9.27)(35.6) = 7114 \text{ Btu}$$

(This value is about 0.5% higher than the 7080 calculated by direct integration in Example 4-4.)

d. Calculate the amount of heat necessary to heat 1 lbmole from 500 to 1000°F.

$$Q = (\bar{C}_{p(1000°)})(1000 - 64.4) - (\bar{C}_{p(500°)})(500 - 64.4)$$

$$= (10.35)(935.6) - (9.74)(435.6) = 4466 \text{ Btu}$$

Let us now see what information is to be gained from these two examples:

1. When an equation of C_p vs. temperature is available, the heat is calculated from

$$Q = \int_{t_1}^{t_2} C_p \, dt$$

2. It is incorrect to choose either the initial or final temperature as the value at which to estimate an average or mean heat capacity. If the heat capacity varies greatly and the temperature range is large, the final answer may be in error by a large amount.

3. In all cases where the heat capacity continues to rise with temperature, the mean heat capacity lies between the values calculated at the initial and final temperatures. The C_p at the arithmetic average temperature may be used if C_p is linear with temperature. Otherwise a mean C_p or actual integration must be used.

4. At the base temperature used in evaluating an equation for the mean heat capacity, the point and mean values are the same.

5. Since the mean heat capacity is based on a certain temperature, its use is limited to calculating amounts of heat necessary to heat a substance *from that temperature to another temperature.* In case the temperature limits do not include the base temperature, it is necessary to calculate the heat to heat the substance from the base temperature to each of the two limits and to subtract (algebraically) one quantity from the other. This is summarized in the equation

$$Q = \bar{C}_{p(t_2)}(t_2 - t_b) - \bar{C}_{p(t_1)}(t_1 - t_b)$$

where t_b represents the base temperature.

6. When one of the temperature limits is close to the base temperature, the error introduced by using the equation

$$Q = \bar{C}_{p(t_2)}(t_2 - t_1)$$

is small. In these examples, the average heat capacity between 100 and 800°F is 10.11, while that between 64.4 and 800°F is 10.12. On the other hand, referring to part *d* of Example 4-5, the use of the simplified equation would yield large errors. The correct amount of heat is 4466 Btu. Using the average value of 9.74 at 500°F would lead to a value of 4870 for the quantity of heat. Use of 10.35 at 1000°F gives 5175 Btu. Both of these are unacceptable.

You have seen from these examples that there are several ways by which to evaluate heat capacities and quantities of heat. In most cases, heat capacities are of little interest in themselves. Their purpose is to enable one to calculate heat quantities. The question naturally arises as to the best method to use when the several alternatives are available. This, of course, depends on the particular problem to be solved—the data available, the accuracy desired, whether the problem must be solved for only one or for many cases, etc. The following problem will illustrate some of these points.

Example 4-6. How much heat is necessary to heat 1 lbmole of CO_2

from 200 to 800°F? The following point values of heat capacity are available:

t°F	0	200	400	600	800	1000
C_p	9.00	9.53	10.04	10.54	11.01	11.45

Solve the problem by several methods, and draw any conclusions that you feel are valid.

a. One method is to fit an equation to the values given and then integrate. A suggested method would be to plot C_p vs. temperature, to see whether all the points seem reliable or whether some of the points are obviously out of line. (Actually, the best method would be the method of least squares, which would give the best statistical fit of the data.) Then the form of the equation to be fitted must be arbitrarily determined. With most gases the three-term polynomial form should be used.

When the data given in this problem are plotted, a smooth curve results. Choosing three temperatures and writing equations for C_p, the constants in the equations may be determined:

$t = 0$: $\quad C_p = 9.00 = a + 0 \times b + 0 \times c$

$t = 400$: $\quad C_p = 10.04 = a + 400b + 400^2c$

$t = 1000$: $\quad C_p = 11.45 = a + 1000b + 1000^2c$

Solving simultaneously,

$$C_p = 9.00 + 2.71 \times 10^{-3}t - 0.256 \times 10^{-6}t^2$$

and

$$Q = \int_{200}^{800} C_p\,dt = (9.00)(800 - 200) + \left(\frac{2.71 \times 10^{-3}}{2}\right)(800^2 - 200^2) - \left(\frac{0.256 \times 10^{-6}}{3}\right)(800^3 - 200^3) = 6170 \text{ Btu}$$

b. If desired, you can derive an equation for mean heat capacity, and use it to calculate heat quantities. From the previous illustration, the equation

$$\bar{C}_p = 9.09 + 1.35 \times 10^{-3}t - 0.0853 \times 10^{-6}t^2$$

was derived for a base temperature of 64.4°F. The solution in tabular form is

Temperature	$\bar{C}_p$	$(\bar{C}_p)(t - 64.4)$
800	10.12	7443
200	9.36	1268

$$Q = 7443 - 1268 = 6175 \text{ Btu}$$

c. The method of graphical integration is always valid. In order to determine the integral of $C_p\,dt$, C_p is plotted on the y axis vs. t on the x axis on rectangular graph paper. A smooth curve is drawn through the points. The area under the curve between the limiting temperatures is the heat. In this problem, if C_p is plotted vs. t on "millimeter" graph paper and the scales are graduated so that 1 cm in the y direction corresponds to one unit of C_p and 1 cm in the x direction corresponds to 100 F°, then each square centimeter has a value of 100×1, or 100 Btu lbmole. The area under the curve between 200 and 800°F is 61.7 squares, and, therefore, $Q = 6170$ Btu.

d. Numerical integration of $C_p\,dt$ is often preferable to graphical integration, since it is less time-consuming. Numerous methods are available. Again it is not within the scope of this text to describe them in any detail. The most convenient and frequently used method is to assume C_p linear in temperature over small temperature ranges. Then, in each range,

$$Q = \bar{C}_p(t_2 - t_1)$$

where $\bar{C}_p = (\frac{1}{2})(C_{p(t_1)} + C_{p(t_2)})$. For example, to heat 1 lbmole from 200 to 400°F,

$$\bar{C}_p = (\tfrac{1}{2})(9.53 + 10.04) = 9.785$$

and $Q = (9.785)(400 - 200) = 1957$ Btu.

The total heat is the sum of all such quantities over the entire range. When the intervals are equal, then

$$Q = (t_2 - t_1)(\tfrac{1}{2})(C_{p(t_1)} + C_{p(t_2)}) + (t_3 - t_2)(\tfrac{1}{2})(C_{p(t_2)} + C_{p(t_3)}) + \cdots$$

or

$$Q = (\Delta t)(\tfrac{1}{2}C_{p(t_1)} + C_{p(t_2)} + \cdots + C_{p(t_{n-1})} + \tfrac{1}{2}C_{p(t_n)})$$

where $C_{p(t_n)}$ is the value at the final temperature. You may recognize this as an example of the "trapezoid rule."

In this problem,

$$Q = (200)\left(\frac{9.53}{2} + 10.04 + 10.54 + \frac{11.01}{2}\right) = 6170 \text{ Btu}$$

e. In some cases, it is advantageous to make a plot of enthalpy vs. temperature. We have shown that

$$\Delta H = \int_{t_1}^{t_2} C_p\,dt$$

along a constant-pressure path. Also, we could say that

$$\Delta H = \bar{C}_p\,\Delta t$$

Establishing any base temperature, we could tabulate or plot H vs. t, where

$$H = \int_{t_b}^{t} C_p \, dt$$

and $H = 0$ when $t = t_b$.

In this problem, for example, we could choose 64.4°F as a base value and use the mean heat capacities already determined. Or we could choose 0°F (or any other temperature). Using 0°F,

$$H = 9.00(t - 0) + \frac{2.71 \times 10^{-3}}{2}(t^2 - 0) - \frac{0.256 \times 10^{-6}}{3}(t^3 - 0)$$

$$H = 9.00t + 1.355 \times 10^{-3}t^2 - 0.0853 \times 10^{-6}t^3$$

Some tabulated values are

t°F	0	200	400	600	800	1000
H Btu/lbmole	0	1853	3811	5869	8024	10,270

Then $Q = 8024 - 1853 = 6171$ Btu.

The example shows several methods of handling the problem. The question now is, "Which one should I use?" The answer is determined by several factors, as mentioned earlier. Certainly the easiest one is illustrated in part *e*, where two factors are chosen from a table or plot, and one value is subtracted from another. This method depends on having the plot available, however, and it may be necessary first to establish the equation for the point or mean heat capacity. The method using the mean heat capacity (part *b*) is also easy, particularly if there is an equation or plot available. The method of analytical integration (part *a*) is simple, again if the equation is available. If it is necessary to fit an equation first, however, in order to use any of these methods, then the methods of graphical or numerical integration (parts *c* and *d*) are preferable.

The conclusions are therefore to use numerical or graphical integration where C_p values are tabulated vs. temperature and where only a few cases are to be solved. Where the solutions to many cases are desired, then it is best to fit an equation to the data. The simplest methods of obtaining heat quantities, based on the availability of an equation for C_p vs. t, are, in order, (1) the use of an enthalpy plot or tabulation, (2) the use of mean heat capacities, and (3) analytical integration.

Constant-volume Heat Capacities. Heat capacities were introduced by the equation

$$dQ = C \, dt \tag{4-23}$$

as a proportionality factor relating rise in temperature and amount of heat. It was stressed that the amount of heat when heating a substance

from one temperature to another is dependent on the path of the process. The illustrations of the past few pages have been devoted to a discussion of C_p, the heat capacity at constant pressure.

Theoretically an infinite number of processes can be devised, thus defining an infinite number of heat capacities for every substance. Only two paths involving the use of heat capacities are of practical importance —constant pressure and constant volume. Thus, for a constant-volume process,

$$dQ = C_v\,dt \tag{4-35}$$

and $Q = \int C_v\,dt$ along a constant-volume path.

For a constant-volume batch process,

$$dU = dQ - dW = dQ \tag{4-20}$$

and thus

$$C_v = \left(\frac{\partial U}{\partial t}\right)_v \tag{4-36}$$

We do not need to discuss the mathematical treatment of C_v in any detail. Methods of expression, conversion, integration, and treating mean values are identical with methods involving C_p. Some attention must be given to numerical values, however, and the relationship of these values to C_p. Consider this problem:

Example 4-7. Liquid water has the following properties:

Property	Saturated liquid	Compressed liquid	Saturated liquid	Compressed liquid
t, °F	32	32	100	100
p, psia	0.08854	0.9492	0.9492	2000
v, ft³/lb	0.016022	.....	0.016132	0.016022
H, Btu/lb	0	0	67.97	73.94

Calculate mean C_p and C_v values between 32 and 100°F.

Solution

a.
$$\bar{C}_p = \frac{\Delta H}{\Delta t} = \frac{67.97 - 0}{100 - 32} = \frac{1.00\ \text{Btu}}{(\text{lb})(\text{F°})}$$

b.
$$\bar{C}_v = \frac{\Delta U}{\Delta t} = \frac{\Delta H - \Delta(pV)}{\Delta t}$$

$$\Delta H = 73.94 - 0 = \frac{73.94\ \text{Btu}}{\text{lb}}$$

$$\Delta(pV) = \left(0.016022\ \frac{\text{ft}^3}{\text{lb}}\right)\left[(2000 - 0.089)(144)\left(\frac{\text{lb}}{\text{ft}^2}\right)\right]\left(\frac{1\ \text{Btu}}{778(\text{ft})(\text{lb})}\right)$$

$$= \frac{5.93\ \text{Btu}}{\text{lb}}$$

Therefore,
$$\bar{C}_v = \frac{73.94 - 5.93}{100 - 32} = 1.00\ \frac{\text{Btu}}{(\text{lb})(\text{F°})}$$

The problem illustrates numerically a statement which is acceptable in practically all engineering applications: *For liquids and solids the heat capacities at constant pressure and at constant volume may be assumed equal.* (This statement may become invalid at extremely high pressures.)

Note in the problem solution that, in calculating $\bar{C}_p$, H values were chosen *at the same pressure;* in calculating $\bar{C}_v$, U values were chosen *at the same specific volume.* Reasonably small pressure changes have little effect on the enthalpy of a liquid or solid and usually do not affect the specific volume appreciably. Both values given for 32°F are the same, within the accuracy of the available tables, and for the number of significant figures carried. On the other hand, the two H values for 100°F are quite different; in this case the two pressures are essentially zero and 1 ton/in.^{2}.

The situation with gases is quite different. There is a distinct difference between the heat capacities at constant pressure and constant volume. Consider these cases:

Example 4-8. A perfect gas with a mean heat capacity of $\bar{C}_p$ is heated from T_1 to T_2. Calculate $\bar{C}_v$ for this gas; i.e., find a relationship between the heat capacities at constant volume and constant pressure.

Solution

Basis: 1 mole. If the gas is heated at constant pressure,

$$\Delta U = Q - W = \bar{C}_p \Delta T - W = \Delta H - W$$

$$W = \int p\, dV = p\, \Delta V = p\Delta\left(\frac{RT}{p}\right) = R\, \Delta T$$

Therefore, $\Delta U = (\bar{C}_p - R)\, \Delta T$ *for a constant-pressure path*

If the gas is heated at constant volume,

$$\Delta U = Q - W = Q = \bar{C}_v\, \Delta T \qquad \textit{for a constant-volume path}$$

In order to answer the question, we must state here another property of perfect gases: *The internal energy and enthalpy of perfect gases are functions of temperature only and are in no way dependent on pressure.*

On the basis of this statement and the above equations,

$$\Delta U = \bar{C}_v\, \Delta T = (\bar{C}_p - R)\, \Delta T$$

regardless of pressure changes. Thus,

$$\bar{C}_v = \bar{C}_p - R \tag{4-37}$$

On a differential basis,

$$dU = C_v\, dt = dH - d(pV) = (C_p - R)\, dT$$

and

$$C_v = C_p - R \tag{4-38}$$

The relationship between C_v and C_p is valid for perfect gases only.

Real gases show varying effects of pressure on internal energy and enthalpy. For most practical cases we will assume the relationship to hold. Even at worst it is a fairly safe method of estimating C_v from C_p data.

Example 4-9. CO_2 at low pressure has a heat capacity, in Btu/(lb mole)(F°), of

$$C_p = 9.00 + 2.71 \times 10^{-3}t - 0.256 \times 10^{-6}t^2$$

For both constant-pressure and constant-volume heating from 0 to 200°F in a batch process, calculate Q, W, ΔU, and ΔH.

Solution

Basis: 1 mole

a. Constant-pressure heating:

$$Q = \Delta H = \int_0^{200} C_p\,dt$$

$$Q = (9.00)(200 - 0) + \left(\frac{2.71 \times 10^{-3}}{2}\right)(200^2 - 0^2) - \left(\frac{0.256 \times 10^{-6}}{3}\right)(200^3 - 0^3)$$

$$Q = 1854 \text{ Btu}$$

$$W = p\,dV = p\,\Delta V = R\,\Delta T$$

$$W = (1.99)(200 - 0) = 398 \text{ Btu}$$

$$\Delta U = Q - W = 1456 \text{ Btu}$$

b. Constant-volume heating. Since U and H depend on temperature only,

$$\Delta U = 1456 \text{ Btu}$$

and

$$\Delta H = 1854 \text{ Btu}$$

At constant volume,

$$W = 0$$

$$Q = \Delta U = 1456 \text{ Btu}$$

We may also calculate Q from

$$Q = \int C_v\,dt$$

since

$$C_v = C_p - R = C_p - 1.99$$

$$C_v = 7.01 + 2.71 \times 10^{-3}t - 0.256 \times 10^{-6}t^2$$

Latent Heat. The discussions of the past few pages have dealt with sensible heat, the heat associated with a change in temperature of a substance without a change in phase. Another important heat quantity is *latent heat*, the heat associated with a change in phase without a change in temperature.

The most common examples of phase change are the melting of a solid, the vaporization of a liquid, or the change of a solid from one crystalline

structure to another. All these processes occur at constant temperature (and pressure, in the case of pure substances), and each has its own characteristic heat effect. These heat effects are known as *heat of fusion* (melting of a solid), *heat of vaporization* (vaporization of a liquid), and *heat of transition* (change of one solid phase to another, such as monoclinic to rhombic sulfur). Occasionally a solid, such as carbon dioxide (dry ice), will vaporize directly to the gaseous phase, a process called *sublimation*. The heat effect associated with this is called the *heat of sublimation*.

It is not within the scope of this text to consider methods of correlation of latent heats. Many theoretical and empirical equations are available. The origin and use of these relations are best considered in a course in physical chemistry.

We are interested at this point, however, in how to *use* latent-heat quantities. Let us first consider which variables of those we have studied are the important ones in this case.

For the present we shall consider phase changes of *pure substances* only. In such a case the melting, transition, sublimation, and boiling points are dependent on only one variable. This variable can be either temperature or pressure. If one is arbitrarily chosen, the other is fixed. For example, when we say the boiling point of water is 212°F, we mean that water boils at this temperature when the pressure is 1 atm. If another pressure is chosen, say 50 psia, the water boils at a different temperature, in this case 281°F. Thus we may state that latent heats are functions of temperature or pressure, but not of both, when we are considering a pure substance.

When a substance is heated or cooled, this process may continue for some time with a steady change in temperature and no phase change. When a *saturation* condition is reached, as for example 212°F at 1 atm in the case of water, the phase change occurs at *constant temperature and pressure*. From the previous equations, we may say that the heat effect is properly represented by a *change in enthalpy*, or

$$Q = \Delta H \tag{4-21}$$

For purposes of identification, the symbols for the various latent heats are sometimes given subscripts: ΔH_f for heat of fusion, ΔH_s for sublimation, ΔH_t for transition, and ΔH_v for vaporization. The symbols L, r, Λ, and λ are also sometimes used instead of ΔH.

Appendixes C, F, and J contain tables relating latent-heat quantities, temperature, and pressure for numerous common substances. Let us now consider the use of this reference material in problem solution.

Example 4-10

a. How much heat is needed to convert 1 lb of liquid water at 1 atm and 32°F to steam at 1 atm and 260°F? Use only the following informa-

tion: $\bar{C}_p$ of liquid water is 1 Btu/(lb)(F°), $\bar{C}_p$ of water vapor is 0.47 Btu/(lb)(F°). The ΔH_v at 1 atm (212°F), read from the tables, is 970.3 Btu/lb.

Solution. If the water is heated and converted to steam at constant pressure, we may write

$$Q = \Delta H = (\bar{C}_{p(\text{liq})})(212 - 32) + \Delta H_v + (\bar{C}_{p(\text{vap})})(260 - 212)$$
$$Q = (1)(180) + 970.3 + (0.47)(48) = 1173 \text{ Btu}$$

b. If liquid water at 32°F and 1 atm were assigned an enthalpy of zero, what would be the enthalpy of steam at 1 atm and 260°F?

Solution. Since $Q = \Delta H = H_2 - H_1$, if H_1 (at 32°F) is made zero, then H_2 (at 260°F and 1 atm) is 1173 Btu/lb.

c. Assuming steam to be a perfect gas at low pressures, what is the enthalpy of steam at 260°F and its saturation pressure, 35.4 psia?

Solution. We make use here of the fact that the enthalpy of a perfect gas is a function of the temperature only. In such a case, the enthalpy of steam would be 1173 Btu/lb at 260°F and 35.4 psia. The value read from tables is about 1167 Btu/lb.

d. Assuming that $\bar{C}_p$ for liquid water is 1.0 at 35.4 psia, that the enthalpy of liquid water at 32°F and 35.4 psia is zero, and that the enthalpy of water vapor at 260°F and 35.4 psia is 1167 Btu/lb, calculate the heat of vaporization of water at 35.4 psia.

Solution

$$\Delta H = (\bar{C}_{p\,\text{liq}})(260 - 32) + \Delta H_v = 1167 - 0 = \frac{1167 \text{ Btu}}{\text{lb}}$$

$$\Delta H_v = 1167 - 228 = \frac{939 \text{ Btu}}{\text{lb}}$$

The value read from the tables is 938.7 Btu/lb.

Study the example carefully to make certain you know how each value taken from the tables was found. Note that we treat enthalpy as an additive quantity. Note that the units of enthalpy are energy/mass (Btu/lb, for example) and that sensible heats are obtained as a product of heat capacity and temperature difference, while latent heats are already enthalpy quantities. Another important point brought out in the problem, part *c*, is that, even in the range below 3 atm, steam does not behave as a perfect gas, since its enthalpy is a function of pressure as well as temperature.

Example 4-10 contains a suggestion of the next principle to be explored. In order to avoid complications, the next example considers steam in a region where it may be assumed a perfect gas.

Example 4-11. The enthalpy of liquid water at 32°F and 1 atm pressure or less is 0. The enthalpy of steam at 500°F and 10 psia or less is 1288 Btu/lb. The mean heat capacities of liquid and vapor may be assumed constant at 1.0 and 0.47, respectively. Given the following relationships between pressure and boiling point, calculate the heat of vaporization at these pressures:

p, psia	1	5	10
t_s, °F	101.7	162.2	193.2

where t_s = saturation temperature.

Solution. In each case,

$$\Delta H = (\bar{C}_{p(\text{liq})})(t_s - 32) + \Delta H_v + (\bar{C}_{p(\text{vap})})(500 - t_s)$$

Therefore,

$$\Delta H_v = 1288 - (1)(t_s - 32) - (0.47)(500 - t_s)$$

Substituting values of t_s, we obtain

p, psia	1	5	10
ΔH_v, Btu/lb	1031	999	983

The tabulated values are 1036, 1001, and 982 Btu/lb, respectively.

Example 4-11 illustrates a principle which will be used in practically all the further work in thermophysics and thermochemistry. We should explore its implications thoroughly.

If you will review some of the earlier treatments of the first law, you will recall that, subject to the important restrictions which apply in most cases, we were able to say that a quantity of heat was equal to a change in internal energy or enthalpy. Such equations are useful or purely academic, depending on whether or not we are able to determine changes in U or H. Recalling some of our earlier discussion, the quantities U and H are *properties* of the material under consideration. A property is definitely fixed by the *state* of the system. In most cases, specifying the pressure, temperature, and composition of a system fixes all the properties. Thus, the derived equations are useful, as long as we have a method of finding the relations between U, H, and the quantities p, T, and composition. We have already shown how H may be determined if heat capacities and latent heats are known.

We have also shown that Q depends on the path of a process. However, when we write $Q = \Delta U$ for a constant-volume batch process or $Q = \Delta H$ for a constant-pressure batch process or a flow process, the actual values of ΔU or ΔH are *entirely independent of path*, and thus *any convenient method may be used for calculating the change in these properties. Only the end points of the hypothetical path must agree with the end points*

of the real path being analyzed. We might draw a fairly accurate analogy between this and material-balance problems. You can solve any material-balance problem, given enough end conditions; the actual size, shape, and type of equipment, and internal conditions, which certainly determine the path of a process, do not enter into the stoichiometric calculations.

Practically, what does the above discussion mean? It means that, once you have established in a problem that Q is ΔU or ΔH, you may choose any path by which to evaluate the change in U or H; when several paths are possible, you choose the one which is easiest to evaluate or the one which gives the most accurate results.

The following examples illustrate the use of this principle:

Example 4-12. One pound of ice at 32°F and 5 lb of water at 80°F are mixed and allowed to stand in an open container in a room. Eventually all the ice melts and the entire mixture is at 70°F. How much heat is added to (or removed from) the water and ice? The heat of fusion is 80 cal/g.

Solution. The process is constant-pressure batch. Therefore $Q = \Delta H$, and the heat added to or removed from the ice and water may be calculated by finding the ΔH. Let us consider two paths.

a. We may assume that the ice and water are mixed with no addition of heat. After they reach an equilibrium temperature we may then heat (or cool) the 6 lb of water to 70°F. (This assumes that all the ice is melted.) In this case, for the mixing without heat transfer with the surroundings,

$$\Delta H = 0 = \Delta H_{\text{ice}} + \Delta H_{\text{water}}$$

$$(\text{wt ice})[\Delta H_f + (\bar{C}_p)(t - 32)] + (\text{wt water})(\bar{C}_p)(t - 80) = 0$$

$$(1)\left[\left(\frac{80 \text{ cal}}{\text{g}}\right)\left(\frac{1.8 \text{ Btu/lb}}{\text{cal/g}}\right) + (1)(t - 32)\right] + (5)(1)(t - 80) = 0$$

From this, t = equilibrium temperature = 48°F.

Now, to heat the water to 70°F,

$$\Delta H = (6 \text{ lb})\left(\frac{1 \text{ Btu}}{(\text{lb})(\text{F}^\circ)}\right)(70 - 48)\ \text{F}^\circ = 132 \text{ Btu}$$

For the two steps,

$$\Delta H = 0 + 132 = 132 \text{ Btu} = Q = \text{heat added to the system}$$

b. Assume the ice and water brought independently to 70°F.

For the ice: $\Delta H = \Delta H_f + (1)(70 - 32) = 182$ Btu

For the water: $\Delta H = (5)(1)(70 - 80) = -50$ Btu

Over-all: $\Delta H = 182 - 50 = 132$ Btu $= Q =$ heat added to system

Example 4-13. Using the fact that the enthalpy of a perfect gas

depends on temperature only and not on pressure, prove that C_p and C_v are also functions of temperature only.

Solution. Assume that 1 lbmole of a perfect gas is heated from T_1 to T_2, at some pressure, p_2, where the C_p is unknown. We know that, at p_2,

$$\Delta H_{p_2} = \int_{T_1}^{T_2} C_{p_2} dT$$

We may choose any path by which to evaluate ΔH_{p_2}. Assuming that C_p is known at pressure p_1, we may follow this path:

1. Change the pressure isothermally at T_1 from p_2 to p_1. $\Delta H = 0$ for this step.
2. Heat the gas from T_1 to T_2 at pressure p_1.

$$\Delta H_{p_1} = \int_{T_1}^{T_2} C_{p_1} dT$$

3. Change the pressure at constant T_2 from p_1 to p_2. $\Delta H = 0$. Since we have gone from p_2, T_1 to p_2, T_2 by three steps, the sum of the ΔH's for these steps is also ΔH_{p_2} (note that the end points are the same). Thus

$$\Delta H_{p_1} = \Delta H_{p_2} = \int_{T_1}^{T_2} C_{p_1} dT = \int_{T_1}^{T_2} C_{p_2} dT$$

Thus we may conclude that $C_{p_1} = C_{p_2}$, or C_p is independent of pressure for a perfect gas. Since, for perfect gases, $C_v = C_p - R$, we have also shown that C_v is independent of pressure.

THERMOCHEMISTRY

The chapter up to this point has been devoted to a discussion of physical changes—the heat and work effects associated with changes in temperature, pressure, and phase of pure substances or of constant-composition mixtures. We have shown that, for most cases of importance, certain simplified equations are of sufficient accuracy; the usefulness and limitations of these equations have been described in detail.

We need now to consider cases where chemical reactions take place. In order to do this, let us first review some of the basic equations. For batch, or nonflow, processes we have the equation $\Delta E = Q - W$. When potential, kinetic, and other miscellaneous forms of energy are absent (or at least do not change), we may substitute internal energy for total energy. This gives us the equation $\Delta U = Q - W$. Q and W are terms which have already been carefully defined; they represent energy interchange with the surroundings. ΔU represents the change in the internal energy of the system between *two times*. A careful look at the derivation of the equation should reveal that it is valid for any type of batch process, *whether the changes occurring are chemical or physical in nature*. Thus we

may immediately state the equations for the practical cases of interest:

For a constant-volume batch process with no work

$$Q = \Delta U \tag{4-20}$$

For a constant-pressure batch process with no work

$$Q = \Delta H \tag{4-21}$$

Similar reasoning, applied to steady-state flow processes, leads to the equation $Q' - W_f' = \Delta H$, where the Q' and W_f' are exactly as previously defined. Again, when there is no flow shaft work,

$$Q' = \Delta H \tag{4-25}$$

It is important to note here that ΔH represents an enthalpy change *with position*, i.e., a difference between two enthalpies at different places within a process flow line.

Knowing that the above equations may be used for both physical and chemical changes, you may logically ask what information is needed in order to solve problems. Suppose that we analyze a simple process to establish the nature of the desired information.

Example 4-14. What heat effect is associated with the burning of (*a*) carbon and (*b*) sulfur?

Solution. The question as stated lacks most of the information needed for a numerical solution. Let us reason out these missing items and make suitable assumptions:

1. The process is not stated. Since the heat effect may be either an internal-energy or an enthalpy change, we must establish the path. Assume a constant-pressure batch process.

2. Initial states are not given. Carbon may exist in numerous states, such as diamond, graphite, coke, and lampblack. Assume that we are burning graphite. Sulfur may exist as one of several solid states, as liquid, or as vapor. Assume solid rhombic sulfur. In addition to the structure or phase of the sulfur and carbon, we must know the initial temperature and pressure. Assume 25°C and 1 atm pressure.

3. The oxygen source and state are not given. We could use pure oxygen or air, or perhaps some other combination of oxygen and nonreacting gas. The relative amount of oxygen must also be given. Assume the stoichiometric amount of pure oxygen gas at 1 atm and 25°C.

4. The final temperature is not given. (Pressure is given in defining the process as constant-pressure batch.) Assume that heat is added or removed so that the final temperature is also 25°C.

5. The products and degree of completion of the reaction are not given. Both carbon and sulfur form more than one oxidation product. Assume that all the carbon forms CO_2 and all the sulfur forms SO_3.

6. Amounts are not stated. Assume 1 gmole of carbon and 1 gmole of sulfur.

From the above it is evident that the statement of the problem should be as follows: What heat effect is associated with the burning of 1 gmole of (*a*) carbon and (*b*) sulfur when both the products and reactants are at 25°C and 1 atm? The process is constant-pressure batch. The carbon is initially in the form of graphite, and the sulfur is solid rhombic crystals. The stoichiometric amount of pure oxygen is used. Both the carbon and sulfur are completely oxidized to their highest oxidation states, that is, CO_2 and SO_3.

The problem is now completely defined and may be solved. First, from the type of process and the restrictions placed upon it, we may write

$$Q = \Delta H$$

Next, we should write the chemical equation:

$$C + O_2 = CO_2$$

This is adequate to define the reaction, but from the standpoint of solving thermochemical problems, it should be written as follows:

$$C(\text{graphite, 1 atm, 25°C}) + O_2(g, \text{ 1 atm, 25°C}) = CO_2(g, \text{ 1 atm, 25°C})$$

In this equation the symbol g is used to indicate the gaseous state. (Similarly we shall use s for solid and l for liquid.) The heat effect is now calculated from an enthalpy change:

$$\Delta H = H \text{ of } CO_2(g, \text{ 1 atm, 25°C}) - H \text{ of } C(\text{graphite, 1 atm, 25°C}) - H \text{ of } O_2(g, \text{ 1 atm, 25°C})$$

The analysis has reduced the problem to one of determining the enthalpies of C, O_2, and CO_2 at the stated conditions. These may be determined only by experiment. Fortunately, all the basic experimental work has been done, and numerical results are tabulated. Some of these results are listed in Appendix G as *heats of formation. The heat of formation of a substance is the enthalpy change associated with a reaction when the reactants are initially in their elemental form at some specified temperature and pressure and the products are obtained at the same temperature and pressure.* The usual conditions of temperature and pressure are 18, 20, or 25°C, and 1 atm, since these are closest to "room conditions" and thus easily attainable in the laboratory. Heats of formation obtained under these "standard" conditions are usually called *standard heats of formation.*

Now you see that you are asked for nothing more than the heat of formation of CO_2, at 1 atm and 25°C. From the table, the value is −94,052 cal/gmole.

The same analysis applies to the heat effects from burning sulfur. In this case the thermochemical equation is

$$S(\text{rhombic, 1 atm, 25°C}) + {}^3\!/_2 O_2(g, \text{ 1 atm, 25°C}) = SO_3(g, \text{ 1 atm, 25°C})$$

From the table, the standard heat of formation of SO_3 is $-94{,}390$ cal/gmole.

In both cases the ΔH is negative. Since $Q = \Delta H$, Q is negative. According to definition, heat is released when Q is negative. You know that this is correct, since both of these are oxidation (combustion) reactions, and heat should be given off.

If the heat of reaction, equal to the heat of formation of CO_2 (or SO_3), in the problem is also equal to the difference in enthalpies of CO_2 (or SO_3) and the elements, it is clear that pure elemental substances must be assigned enthalpy values of zero. Reference to the table shows that oxygen, graphite, and rhombic sulfur all have zero enthalpy at 1 atm and 25°C. These values are set at zero *by definition*. In making heat balances we are always interested in enthalpy *changes*. Calculations are simplified by making as many values as possible equal to zero.

Next, let us consider a problem where compounds appear on both sides of the equation.

Example 4-15. What heat effect is associated with the burning of 1 gmole of CO to CO_2 with the stoichiometric amount of pure oxygen in a constant-pressure-batch process at 1 atm and 25°C?

Solution. For this process, $Q = \Delta H$. From the reaction,

$$CO(g, \text{ 1 atm, 25°C}) + {}^1\!/_2 O_2(g, \text{ 1 atm, 25°C}) = CO_2(g, \text{ 1 atm, 25°C})$$

$$\Delta H = H \text{ of } CO_2(g, \text{ 1 atm, 25°C}) - H \text{ of } CO(g, \text{ 1 atm, 25°C}) - {}^1\!/_2 H \text{ of } O_2(g, \text{ 1 atm, 25°C})$$

We have already stated that, at standard conditions, enthalpies in this equation are enthalpies of formation. Thus

$$\Delta H_r = \Delta H_f \text{ of } CO_2 - \Delta H_f \text{ of } CO - {}^1\!/_2 \Delta H_f \text{ of } O_2$$

(using subscripts r for "reaction" and f for "formation"). From the table,

$$\Delta H_r = -94{,}052 - (-26{,}416) - 0 = \frac{-67{,}636 \text{ cal}}{\text{gmole}}$$

Again the enthalpy change, equal to heat added, is negative; thus heat is evolved, as must be true for a combustion reaction.

Now let us consider some of the implications of the example. Since ΔH_f of O_2 is zero,

$$\Delta H_r = \Delta H_f \text{ of } CO_2 - \Delta H_f \text{ of } CO$$

Suppose that we write the chemical equations for the formation of CO and CO_2:

$C(\text{graphite, 1 atm, 25°C}) + \frac{1}{2}O_2(g, \text{1 atm, 25°C}) = CO(g, \text{1 atm, 25°C})$
$C(\text{graphite, 1 atm, 25°C}) + O_2(g, \text{1 atm, 25°C}) = CO_2(g, \text{1 atm, 25°C})$

Dropping the descriptive terms, reverse the first equation and add:

$$\begin{array}{r} CO = C + \frac{1}{2}O_2 \\ C + O_2 = CO_2 \\ \hline CO + \frac{1}{2}O_2 = CO_2 \end{array}$$

The sum is the desired reaction. ΔH for the first reaction is $-\Delta H_f$ of CO; that for the second is ΔH_f of CO_2. If we add these, we obtain

$$\Delta H_r = \Delta H_f \text{ of } CO_2 - \Delta H_f \text{ of CO}$$

We have just illustrated one of the most important principles of thermochemistry: *When a desired chemical reaction can be written as a sum of two or more other reactions, the enthalpy change for the reaction is the sum of the enthalpy changes of the reactions which have been added.*

When adding chemical reactions, it is essential to carry along the information about the temperature, pressure, and phase composition. In the preceding discussion, the terms "*g*, 1 atm, 25°C" were dropped only after there was no possibility of confusion.

When the heat of formation was introduced, we described the "standard" heat of formation and defined it as an enthalpy change associated with the formation of a compound from its elements. Pressure and temperature conditions of both the reactants and products were definitely fixed. Satisfactory standards, such as 1 atm pressure and "room temperature," were described. The concept of a standard enthalpy change is valid also for reactions such as the one described in Example 4-15, where compounds appear on both sides of the equation. The standard enthalpy change for *any reaction* is called the *standard heat of reaction.* For convenience we may speak of heats of certain types of reaction, such as heat of formation (Example 4-14), heat of combustion (Example 4-15), or heats of isomerization, solution, neutralization, and the like. These special names should not be allowed to confuse the issue; *all of these are heats of reaction.*

The principle that the enthalpy change of any reaction is the sum of the enthalpy changes of all the reactions which may be added to obtain the reaction means that we do not have to measure experimentally the heat of formation of every compound. This is often difficult to do, particularly with organic reactions where numerous products may be obtained from the same reactants. *As long as we know the heat effect of one reaction of each compound appearing in an equation, we can usually calculate the heat effect for the reaction.* In the usual case these heat effects are heats of combustion. Example 4-16 shows the procedure.

Example 4-16. When benzene liquid is completely burned to carbon dioxide and liquid water, the standard heat of combustion is −780,980 cal/gmole. The standard heat of combustion of hydrogen to liquid water is −68,317 cal/gmole, that of carbon to CO_2 is −94,052 cal/gmole. Calculate the standard heat of formation of benzene liquid.

Solution. In equation form the information we have is this:

(1) $C_6H_6(l, 1 \text{ atm}, 25°C) + 15\frac{1}{2}O_2(g, 1 \text{ atm}, 25°C)$
$= 6CO_2(g, 1 \text{ atm}, 25°C) + 3H_2O(l, 1 \text{ atm}, 25°C)$
$\Delta H_c = -780{,}980 \text{ cal}$

(2) $H_2(g, 1 \text{ atm}, 25°C) + \frac{1}{2}O_2(g, 1 \text{ atm}, 25°C)$
$= H_2O(l, 1 \text{ atm}, 25°C) \qquad \Delta H_f = -68{,}317 \text{ cal}$

(3) $C(\text{graphite}, 1 \text{ atm}, 25°C) + O_2(g, 1 \text{ atm}, 25°C)$
$= CO_2(g, 1 \text{ atm}, 25°C) \qquad \Delta H_f = -94{,}052 \text{ cal}$

We should like the heat effect for the reaction

$$6C(\text{graphite}, 1 \text{ atm}, 25°C) + 3H_2(g, 1 \text{ atm}, 25°C) = C_6H_6(l, 1 \text{ atm}, 25°C)$$

Noting that the descriptive terms for each compound or element are the same in all equations, we may drop these terms safely. If we reverse reaction 1, add 3 times reaction 2 and 6 times reaction 3, these should add up to the desired reaction. Then the heat effect of the desired reaction should be the sum of the negative of reaction 1 plus 3 times reaction 2 plus 6 times reaction 3:

$6CO_2 + 3H_2O = 15\frac{1}{2}O_2 + C_6H_6$	$-(-780{,}980)$
$3H_2 + \frac{3}{2}O_2 = 3H_2O$	$3(-68{,}317)$
$6C + 6O_2 = 6CO_2$	$6(-94{,}052)$
$6C + 3H_2 = C_6H_6$	$+11{,}717$

Thus the standard heat of formation of liquid benzene is 11,717 cal/gmole.

Note that we have been careful to specify the pressure, temperature, and *phase* of the various compounds and elements. In some cases this causes little trouble; in most engineering problems oxygen is a gas, for example. However, such materials as water and benzene may be either liquid or vapor within the ordinary range of engineering practice and solids such as sulfur and carbon may easily appear in more than one crystalline structure. Special precautions must be taken in such cases.

Tables of heats of formation and combustion usually contain values for more than one phase in such cases. For water, for example, the heat of formation of liquid water is −68,317 cal/gmole, and the heat of formation of water vapor is −57,798 cal/gmole. Both of these values are for the product (water) at 1 atm and 25°C. For benzene the heats of formation are 11,717 and 19,820 cal/gmole for liquid and gas, respectively. However, a substance cannot exist as both liquid and vapor at a fixed

temperature and pressure, unless it is at its vapor pressure. Thus, for water with a normal boiling point of 100°C and benzene with a normal boiling point of 80.1°C, the only phase which can exist at 25°C is liquid. This means that the values for the heats of formation of liquid water and benzene agree with experimental fact, whereas it would be impossible to form the vapors of these substances under standard conditions. The heats of formation in the vapor phase are obtained by adding the heat of vaporization *at the vapor pressure* and the standard temperature to the standard heat of formation of the liquid. The difference between the heat of formation of the vapor calculated in this manner and the imaginary, or "fictitious," value used in thermochemical calculations amounts to the enthalpy change for compressing a liquid or for changing the pressure on a gas in the range of 1 atm. In both cases this is negligible.

The heat of formation of the liquid is algebraically less (more negative) than that of the vapor. This means that more heat would be released (or less absorbed) from forming a liquid than a vapor; this difference is the heat of vaporization. In the case of combustion of fuels containing hydrogen, the heat of combustion may be reported on the basis of forming liquid or vapor water. The heating value when liquid water is a product is called the *gross* or *higher* heating value; the value when water vapor is a product is called the *net* or *lower* heating value.

Example 4-17. The standard gross heating value of benzene liquid is −780,980 cal/gmole. Calculate the standard net heating value.

Solution

$$\begin{array}{rr} C_6H_6(l) + \dfrac{15O_2}{2} = 6CO_2 + 3H_2O(l) & -780{,}980 \\ 3H_2O(l) = 3H_2O(g) & 3(10{,}519) \\ \hline C_6H_6(l) + \dfrac{15O_2}{2} = 6CO_2 + 3H_2O(g) & -749{,}423 \end{array}$$

Example 4-18. A coal has a standard lower heating value of 13,000 Btu/lb. Chemical analysis shows the coal has 5%w net hydrogen (i.e., hydrogen which is stoichiometrically in excess of the oxygen in the coal). What is the standard higher heating value in Btu/lb?

Solution. Each pound of coal contains 0.05 lb net hydrogen, or 0.025 lbmole. The higher heating value is the lower heating value plus the heat released by condensing 0.025 lbmole of water.

$$(0.025 \text{ lbmole}) \left(\frac{10{,}519 \text{ cal}}{\text{gmole}}\right) \left(\frac{1.8 \text{ Btu/lbmole}}{1 \text{ cal/gmole}}\right) = 473 \text{ Btu}$$

The higher heating value is therefore 13,473 Btu/lb.

Heats of Solution. Up to this point we have considered only standard heat effects. These were restricted to cases where we had pure reactants

and products under carefully specified conditions of temperature, pressure, and phase or structure. Practical cases demand that we consider reactions where reactants and/or products are not at the standard conditions. The heat released or absorbed during a chemical reaction is modified by deviations of temperature, pressure, and composition from the standard values.

One particular heat effect associated with composition is the *heat of solution.* Let us consider an experiment we might run to determine the nature of the heat of solution. Suppose that we put 1 gmole of sulfuric acid into a container surrounded by a constant-temperature bath maintained at the standard temperature and then dilute the sulfuric acid with water. As we do so, heat is released. Following are some data we might obtain from such an experiment:

Total water added	Additional water added	Total heat released	Additional heat released
0		0	
	1		6900
1		6,900	
	1		3100
2		10,000	
	1		1700
3		11,700	
	1		1100
4		12,800	
	1		800
5		13,600	
	1		600
6		14,200	
	2		800
8		15,000	
	2		400
10		15,400	
	5		900
15		16,300	
	5		800
20		17,100	
	∞		1100
∞		18,200	

Now what do these figures mean? The column labeled "Total heat released" is the negative of the *integral heat of solution.* It represents the total heat released when 1 mole of the substance in question is diluted with the amount of water indicated, when both the reactants and products are at standard conditions. The integral heat of solution, being the

negative of the heat released, is the enthalpy change for the solution. As such it may be treated in exactly the same manner as all other heats of reaction. Consider these problems:

Example 4-19

a. What standard heat effect is associated with diluting 1 gmole H_2SO_4 with 10 gmole H_2O?

b. What standard heat effect is associated with diluting a solution containing 1 gmole H_2SO_4 and 1 gmole H_2O with 9 gmole H_2O?

Solution

a. The thermochemical equation may be written

$$H_2SO_4(l,\ 1\text{ atm},\ 25°C) + 10H_2O(l,\ 1\text{ atm},\ 25°C) = H_2SO_4(10H_2O)(l,\ 1\text{ atm},\ 25°C) \qquad \Delta H = \frac{-15{,}400\text{ cal}}{\text{gmole } H_2SO_4}$$

Thus 15,400 cal are released.

b. Dropping "l, 1 atm, 25°C" from the descriptive terms, we write as the desired reaction

$$H_2SO_4(1H_2O) + 9H_2O = H_2SO_4(10H_2O)$$

To obtain this we add two reactions for the solution of pure H_2SO_4.

	ΔH
$H_2SO_4 + 10H_2O = H_2SO_4(10H_2O)$	$-15{,}400$
$H_2SO_4(1H_2O) = H_2SO_4 + H_2O$	$-(-6{,}900)$
$H_2SO_4(1H_2O) + 9H_2O = H_2SO_4(10H_2O)$	$-8{,}500$

The heat released is 8500 cal.

From this illustration we may deduce an important relationship for calculating heats of solution: *The enthalpy change for diluting a solution is the integral heat of solution at the final concentration minus that at the initial concentration.*

Since equations for solution are handled in exactly the same manner as equations for reactions, we need make no distinction between them when calculating heat effects for combined reaction and solution. These examples show how the equations are used.

Example 4-20. The standard heat of formation of sulfuric acid in a solution of 1 mole H_2SO_4 in 400 mole of water (i.e., combined formation and solution) is $-212{,}030$ cal/gmole. The standard heat of dilution of H_2SO_4 in 400 mole of water is $-18{,}340$.

What is the standard heat of formation of pure H_2SO_4?

	ΔH
$H_2 + S + 2O_2 + 400H_2O = H_2SO_4(400H_2O)$	$-212{,}030$
$H_2SO_4(400H_2O) = H_2SO_4 + 400H_2O$	$-(-18{,}340)$
$H_2 + S + 2O_2 = H_2SO_4$	$-193{,}690$

The standard heat of formation of H_2SO_4 is $-193{,}690$ cal/gmole.

Example 4-21. Given the following standard heats of formation,

	cal/gmole
KOH(*c*)	−102,020
KOH(400H_2O)	−114,960
HCl(*g*)	− 22,063
HCl(400H_2O)	− 39,850
KCl(*c*)	−104,348
KCl(400H_2O)	−100,164
H_2O(*l*)	− 68,317

calculate the standard enthalpy changes for the following reactions:

a. KOH + HCl
b. Solution of KOH
c. Solution of HCl
d. Solution of KCl
e. KOH + HCl(400H_2O)

Solution

a. $KOH(c) + HCl(g) = KCl(c) + H_2O(l)$

$$\Delta H = -104{,}348 - 68{,}317 - (-102{,}020) - (-22{,}063)$$
$$\Delta H = -48{,}582 \text{ cal}$$

b. $KOH(c) + 400H_2O = KOH(400H_2O)$

$$\Delta H = -114{,}960 - (-102{,}020) = -12{,}940 \text{ cal}$$

c. $HCl(g) + 400H_2O = HCl(400H_2O)$

$$\Delta H = -39{,}850 - (-22{,}063) = -17{,}787 \text{ cal}$$

d. $KCl(c) + 400H_2O = KCl(400H_2O)$

$$\Delta H = -100{,}164 - (-104{,}348) = +4184 \text{ cal}$$

e. For this part we may add three of the above equations:

	ΔH
$KOH(c) + HCl(g) = KCl(c) + H_2O(l)$	−48,582
$HCl(400H_2O) = HCl(g) + 400H_2O$	−(−17,787)
$KCl(c) + 400H_2O = KCl(400H_2O)$	+4,184
$HCl(400H_2O) + KOH(c) = KCl(400H_2O) + H_2O(l)$	−26,611

Part *e* may also be solved using the information given in the problem:

$$HCl(400H_2O) + KOH(c) = KCl(400H_2O) + H_2O(l)$$
$$\Delta H = -100{,}164 - 68{,}317 - (-39{,}850) - (-102{,}020)$$
$$\Delta H = -26{,}611 \text{ cal}$$

When we calculate heats of solution, the heat of formation of the substance in the initial state is subtracted from that in the final state. In

such problems water may be treated as an element; i.e., its heat of formation *does not* enter the calculation. On the other hand, when water is *formed* (see part *a*) its heat of formation *does* enter the calculation. When water is formed in a solution (see part *e*) the heat of formation of the water *which is formed* must be included in the calculation. For this reason the products may be conveniently written separately, as, for example, $KCl(400H_2O) + H_2O$. The actual product is $KCl(401H_2O)$. Separating the products (on paper) decreases the chances of overlooking the water formed in making calculations.

In the figures in Appendix S we have plotted integral heats of solution vs. mole of water/mole solute. This is the standard method of presenting the data. You will note, in the table of heats of formation, that some heat-of-solution data are included there also.

Occasionally you will see references to *differential heats of solution*. For the purposes of making heat balances, this concept is not of any consequence, and we shall not discuss the subject in this text.

When writing thermochemical equations, always include enough details so that there is no question as to the exact state of each substance in the equation. Part *a* of Example 4-21 is a good illustration. If the question is asked, "How much heat is released (assuming the reaction would take place) when 1 gmole of gaseous HCl reacts with 1 gmole of crystalline KOH?," we should have to have more details about the way in which the reaction is carried out. The answer $\Delta H = -48{,}582$ cal is the standard heat of reaction when crystalline KCl and liquid water are formed *but not mixed*. This is true because we have used thermochemical values based on standard states. In order to determine a value which would be representative of actual conditions, where the products were mixed, the heat of solution would have to be added to the above value.

The same thing is true in regard to gaseous reactions. We shall see that certain heat effects are negligible, which simplifies the calculations greatly. Consider this example:

Example 4-22. When CO and steam are mixed, the reversible reaction

$$CO + H_2O(g) \rightleftharpoons CO_2 + H_2$$

may take place. The degree of completion of the reaction depends on external conditions, primarily temperature.

a. What is the standard heat of reaction when 1 gmole of CO reacts?

b. What is the actual heat of reaction at standard conditions?

Solution

a. $CO(g, 1 \text{ atm}, 25°C) + H_2O(g, 1 \text{ atm}, 25°C)$
$= CO_2(g, 1 \text{ atm}, 25°C) + H_2(g, 1 \text{ atm}, 25°C)$

ΔH_f; $-26{,}416$; $-57{,}798$; $-94{,}052$; 0

Therefore, $\Delta H = -94{,}052 - (-26{,}416) - (-57{,}798) = -9838$ cal

b. If we wish to express the reaction in symbolic form, we should have to write something like this:

Assume that 1 mole CO reacts. Since the reaction does not go to completion but stops at some intermediate stage, assume X mole CO and X mole steam are supplied. Then the reactants are X mole CO and X mole $H_2O(g)$ at 25°C and 1 atm *total* pressure. Thus each has a mole fraction of 0.5. The products are 1 mole CO_2 and 1 mole H_2, each at a mole fraction of $1/(2X)$, plus $(X - 1)$ mole CO and $(X - 1)$ mole $H_2O(g)$, each at a mole fraction of $(X - 1)/(2X)$, at 25°C and 1 atm *total* pressure.

The thermochemical equation from part *a* is

$$CO(S) + H_2O(S) = CO_2(S) + H_2(S)$$

To shorten the expression we have written S, meaning "standard," for "*g*, 1 atm, 25°C." The actual reactants are

$$XCO(m_1) + XH_2(m_1)$$

where m_1 is used to denote initial mixture.

The products are

$$CO_2(m_2) + H_2(m_2) + (X - 1)CO(m_2) + (X - 1)H_2O(m_2)$$

where m_2 is used to denote final mixture.

We may now write three equations:

$$CO(S) + H_2O(S) = CO_2(S) + H_2(S)$$

$$XCO(m_1) + XH_2(m_1) = XCO(S) + XH_2O(S)$$

and

$$(X - 1)CO(S) + (X - 1)H_2O(S) + CO_2(S) + H_2(S) = (X - 1)CO(m_2) + (X - 1)H_2O(m_2) + CO_2(m_2) + H_2(m_2)$$

When these are added together, we obtain the equation

$$XCO(m_1) + XH_2(m_1) = (X - 1)CO(m_2) + (X - 1)H_2O(m_2) + CO_2(m_2) + H_2(m_2)$$

which represents symbolically the reaction as it actually occurs. The enthalpy change for the reaction is thus the sum of the standard enthalpy change plus the changes for preparing the initial and final mixtures from gases in the standard states. We shall make the assumption that *the enthalpy change for mixing gases is negligible*. The change is zero for perfect gases and negligible for most gases under ordinary commercial conditions. It becomes important only when the gases approach critical conditions.

Thus, for part *b* also, $\Delta H = -9838$ cal.

Example 4-23. A process requires 1000 lb/hr of 20% w H_2SO_4. This is made by diluting commercial 78% w acid with water.

a. How much concentrated acid and water are used per hour?

b. How much heat must be added or removed per hour?

Solution

a. Basis 100 lb 20% acid. If C = weight of concentrated acid,

$$0.78C = (0.20)(100) \qquad C = 25.65 \text{ lb}$$

If W = weight of water,

$$W = 100 - 25.65 = 74.35 \text{ lb}$$

Therefore 256.5 lb acid and 743.5 lb water are needed per hour.

b. To calculate heat requirements, we must first find integral heats of solution. Since no temperatures are given, standard conditions of 25°C must be assumed.

$$\text{Inlet acid: } \frac{22}{18} \div \frac{78}{98} = \frac{1.54 \text{ mole } H_2O}{\text{mole } H_2SO_4} \qquad \Delta H_s = \frac{-9000 \text{ cal}}{\text{gmole}}$$

$$\text{Outlet acid: } \frac{80}{18} \div \frac{20}{98} = \frac{21.8 \text{ mole } H_2O}{\text{mole } H_2SO_4} \qquad \Delta H_s = \frac{-17{,}500 \text{ cal}}{\text{gmole}}$$

Basis: 1 gmole H_2SO_4

	ΔH
$H_2SO_4(1.54H_2O) \rightarrow H_2SO_4 + 1.54H_2O$	$-(-9000)$
$H_2SO_4 + 21.8H_2O \rightarrow H_2SO_4(21.8H_2O)$	$-17{,}500$
$H_2SO_4(1.54H_2O) + 20.3H_2O \rightarrow H_2SO_4(21.8H_2O)$	$-8{,}500$

$$\text{Acid used per hour} = \frac{256.5}{98} = \frac{2.62 \text{ lbmole}}{\text{hr}}$$

$$\text{Therefore, } \Delta H = \left(\frac{-8500 \text{ cal}}{\text{gmole}}\right)\left(\frac{\text{Btu}}{\text{cal/gmole}}\right)\left(\frac{1.8 \text{ lbmole}}{\text{lbmole}}\right)\left(\frac{2.62 \text{ lbmole}}{\text{hr}}\right)$$

$$= \frac{-40{,}100 \text{ Btu}}{\text{hr}}$$

Since ΔH is negative, 40,100 Btu are *released* per hour.

Example 4-24. A process requires 1000 lb/hr of 20%w HCl gas in nitrogen. This is made by diluting a stream of 78%w HCl in nitrogen with pure nitrogen.

a. How much concentrated gas and nitrogen are used per hour?

b. If perfect gases are assumed, how much heat must be added or removed per hour?

Solution

a. The solution is exactly the same as for Example 4-23. Therefore 256.5 lb of the 78% stream and 743.5 lb pure nitrogen must be used per hour.

b. Enthalpy changes for mixing perfect gases are zero. Therefore no heat effect is present.

You should make several observations from the above examples:

1. The method of calculating the material balance is independent of the actual materials being handled. In this case, with identical compositions specified, the answers are numerically equal.

2. The basic equation for heat balances is the same in both cases, i.e.,

$$Q = \Delta H$$

The general method of obtaining enthalpy changes from arbitrarily chosen paths is also the same. However, the answers depend on the type of material being processed and so are *not* numerically the same.

3. The two blending operations would obviously be carried out in different types of equipment. Stoichiometric and thermodynamic calculations are of no value in determining types or sizes of equipment. Once a type is chosen for an operation (this is usually a matter of experience and economics), the proper size is determined from "kinetic" calculations. This material is studied in unit operations.

In the section on thermophysics we discussed methods of calculating enthalpy changes for pure gases. We also stated that, for perfect gases, the heat capacity was independent of pressure and dependent only on temperature. We avoided a discussion of gas mixtures, however. With the aid of the above discussion on enthalpy changes for mixing gases, we may now show the method to be used in calculating enthalpy changes for heating gas mixtures.

Example 4-25

a. Show that the molal heat capacity of a mixture of perfect gases (n_A mole of A, n_B mole of B, $\cdots$) is $y_A C_{p_A} + y_B C_{p_B} + \cdots$, where y represents mole fraction.

b. Derive an equation for the heat capacity of a mixture when each individual heat capacity is expressed as a quadratic function of temperature.

Solution

a. If we heated the gases individually, each gas being in a pure state at 1 atm,

$$\Delta H = n_A \int_{t_1}^{t_2} C_{p_A}\, dt + n_B \int_{t_1}^{t_2} C_{p_B}\, dt + \cdots$$

We wish instead to find a heat capacity of the mixture, C_{p_m}, such that

$$\Delta H = (n_A + n_B + \cdots) \int_{t_1}^{t_2} C_{p_m}\, dt$$

Let us write separate equations for each component:

$$n_A(g, 1 \text{ atm}, t_1) = n_A(g, 1 \text{ atm}, t_2) + \Delta H_{A_1}$$

$$n_B(g, 1 \text{ atm}, t_1) = n_B(g, 1 \text{ atm}, t_2) + \Delta H_{B_1}, \text{ etc.}$$

$$(n_A + n_B + \cdots)(\text{mixed } g, 1 \text{ atm}, t_1) = n_A(g, 1 \text{ atm}, t_1) + n_B(g, 1 \text{ atm}, t_1) + \cdots + \Delta H_2$$

$$n_A(g, 1 \text{ atm}, t_2) + n_B(g, 1 \text{ atm}, t_2) + \cdots = (n_A + n_B + \cdots)(\text{mixed } g, 1 \text{ atm}, t_2) + \Delta H_3$$

Adding these equations, we obtain

$$(n_A + n_B + \cdots)(\text{mixed } g, 1 \text{ atm}, t_1) = (n_A + n_B + \cdots)(\text{mixed } g, 1 \text{ atm}, t_2) + \Delta H$$

which represents the process symbolically. We now define a mixed heat capacity C_{p_m}. Adding enthalpies for the three equations, we find two of them are for mixing of gases and are therefore zero. Thus the enthalpy change for heating the mixture is the same as that for heating the gases individually. We may therefore say

$$(\Sigma n) \int_{t_1}^{t_2} C_{p_m}\, dt = n_A \int_{t_1}^{t_2} C_{p_A}\, dt + n_B \int_{t_1}^{t_2} C_{p_B}\, dt + \cdots \tag{4-39}$$

where $\Sigma n = n_A + n_B + \cdots$.

Dividing by Σn and noting that

$$y_A = \frac{n_A}{\Sigma n}$$

we have $$C_{p_m} = y_A C_{p_A} + y_B C_{p_B} + \cdots = \Sigma y_i C_{p_i} \tag{4-40}$$

as was to be proved.

b. If each heat capacity is written in a form

$$C_{p_i} = a_i + b_i t + c_i t^2 \tag{4-32}$$

and $$C_{p_m} = \Sigma y_i C_{p_i}$$

then $$C_{p_m} = (y_A a_A + y_B a_B + \cdots) + (y_A b_A + y_B b_B + \cdots)t + (y_A C_A + y_B C_B + \cdots)t^2$$

or $$C_{p_m} = \Sigma y_i a_i + (\Sigma y_i b_i)t + (\Sigma y_i c_i)t^2 \tag{4-41}$$

Example 4-26. Flue gases leaving a stack at 450°F have an over-all molar composition of 8.2% CO_2, 2.7% CO, 2.7% H_2O, 9.4% O_2, and 77.0% N_2. Calculate the heat lost in 100 mole of this gas, above 25°C (assuming water in the vapor form), using

a. Quadratic heat-capacity equations

b. A mixed mean heat capacity

Solution a. For the equation

$$C_p = a + bT + cT^2$$

the constants are

Gas	a	$b \times 10^3$	$c \times 10^6$
CO_2	7.70	5.3	−0.83
CO	6.60	1.2	
H_2O	8.22	0.15	1.34
O_2	6.76	0.61	0.13
N_2	6.76	0.61	0.13

In the equation, C_p = cal/(gmole)(K°) and T = °K. For review, we shall solve the problem in two ways.

First: $dQ = dH = (\Sigma na)\,dT + (\Sigma nb)T\,dT + (\Sigma nc)T^2\,dT$

or $$Q = (\Sigma na)(T_2 - T_1) + (\Sigma nb)\left(\frac{T_2^2 - T_1^2}{2}\right) + (\Sigma nc)\left(\frac{T_2^3 - T_1^3}{3}\right)$$

Working with the equations in the units given, assume 100 gmole of gas A tabular solution is best.

Gas	n	a	na	$b \times 10^3$	$nb \times 10^3$	$c \times 10^6$	$nc \times 10^6$
CO_2.....	8.2	7.70	63.14	5.30	43.46	−0.83	−6.81
CO.....	2.7	6.60	17.82	1.20	3.24		
H_2O....	2.7	8.22	22.19	0.15	0.41	1.34	3.62
O_2.....	9.4	6.76	63.54	0.61	5.73	0.13	1.22
N_2.....	77.0	6.76	520.52	0.61	46.97	0.13	10.01
			687.21		99.81		8.04

Therefore

$$Q = 687.21(T_2 - T_1) + \frac{99.81 \times 10^{-3}}{2}(T_2^2 - T_1^2) + \frac{8.04 \times 10^{-6}}{3}(T_2^3 - T_1^3)$$

$T_1 = 298°\text{K}$

$T_2 = 506°\text{K}\ (450°\text{F})$

Therefore

$$Q = (687.21)(506 - 298) + (49.91 \times 10^{-3})(506^2 - 298^2) + (2.68 \times 10^{-6})(506^3 - 298^3)$$

$$Q = 142{,}940 + 8350 + 276 = \frac{151{,}570 \text{ cal}}{100 \text{ gmole}}$$

$$\left(\frac{151{,}570 \text{ cal}}{100 \text{ gmole}}\right)\left(\frac{1.8 \text{ Btu/lbmole}}{\text{cal/gmole}}\right) = \frac{272{,}820 \text{ Btu}}{100 \text{ lbmole}}$$

We may also approach the problem by converting each equation to the English units or by converting the final equation. The method is adequately illustrated by the latter.

The mixed heat capacity is

$$C_{p_m} = 6.87 + 0.998 \times 10^{-3}T + 0.0804 \times 10^{-6}T^2$$

in the original units. Convert each term:

$$\left(\frac{6.87 \text{ cal}}{(\text{gmole})(\text{K}^\circ)}\right)\left(\frac{\text{Btu}/(\text{lbmole})(\text{R}^\circ)}{\text{cal}/(\text{gmole})(\text{K}^\circ)}\right) = \frac{6.87 \text{ Btu}}{(\text{lbmole})(\text{R}^\circ)}$$

$$\left(\frac{0.998 \times 10^{-3} \text{ cal}}{(\text{gmole})(\text{K}^\circ)(^\circ\text{K})}\right)(1)\,[(t + 460)^\circ\text{R}]\left(\frac{(^\circ\text{K})}{1.8^\circ\text{R}}\right)$$

$$= \left(\frac{0.554 \times 10^{-3} \text{ Btu}}{(\text{lbmole})(\text{R}^\circ)(^\circ\text{F})}\right)(t^\circ\text{F}) + \left(\frac{0.255 \text{ Btu}}{(\text{lbmole})(\text{R}^\circ)}\right)$$

$$\left(\frac{0.0804 \times 10^{-6} \text{ cal}}{(\text{gmole})(\text{K}^\circ)(^\circ\text{K})^2}\right)(1)\,[(t + 460)^\circ\text{R}]^2\left(\frac{^\circ\text{K}}{1.8^\circ\text{R}}\right)^2$$

$$= \left(\frac{0.0248 \times 10^{-6} \text{ Btu}}{(\text{lbmole})(\text{R}^\circ)(^\circ\text{F})^2}\right)(t^\circ\text{F})^2 + \left(\frac{0.0228 \times 10^{-3} \text{ Btu}}{(\text{lbmole})(\text{R}^\circ)(^\circ\text{F})}\right)(t^\circ\text{F}) + \frac{0.0053 \text{ Btu}}{(\text{lbmole})(\text{R}^\circ)}$$

Therefore in English units, with t in °F,

$$C_{p_m} = 7.13 + 0.577 \times 10^{-3}t + 0.0248 \times 10^{-6}t^2$$

In this problem, for 100 lbmole,

$$\frac{Q}{100} = (7.13)(4.50 - 77) + \left(\frac{0.577 \times 10^{-3}}{2}\right)(450^2 - 77^2) + \left(\frac{0.0248 \times 10^{-6}}{3}\right)(450^3 - 77^3)$$

$$Q = (100)(2667 + 55 + 1) = 272{,}300 \text{ Btu}$$

The answers differ slightly in the last figure, which is beyond slide-rule accuracy.

Solution b. The mixed mean heat capacity is

$$\bar{C}_{p_m} = y_A\bar{C}_{p_A} + y_B\bar{C}_{p_B} + \cdots$$

From plots of mean heat capacity between "room temperature" and t°F, we make the calculation in tabular form:

Gas	y	C_p (77 to 450°F)	$y\bar{C}_p$
CO_2	0.082	9.8	0.804
CO	0.027	7.1	0.192
H_2O	0.027	8.2	0.221
O_2	0.094	7.2	0.677
N_2	0.770	7.0	5.39
Mixed mean heat capacity = $\bar{C}_{p_m}$ =			7.284

$$Q = (100)(7.284)(450 - 77) = 272{,}000 \text{ Btu}$$

For the past few pages we have been considering reactions carried out

at constant temperature and pressure All tables of heats of reaction (including formation, combustion, solution, etc.), with few exceptions, are based on these conditions. The constant-pressure constant-temperature reaction is industrially important. However, there are other cases which are important in the laboratory and plant, and we need to explore these before concluding our discussion.

Constant-volume Relations. It is interesting to note that many heat-of-reaction data are not obtained at standard conditions of constant pressure and temperature; thus the heat released or absorbed is not the enthalpy change for the reaction. Some adjustment must be made in the values before they can be reported as enthalpy changes.

The most commonly used piece of equipment for measuring heat effects, primarily heats of combustion, is the *Parr bomb*. This consists of a strong metal container surrounded by another container filled with water. The entire system is carefully insulated from the surroundings. The material whose heat of combustion is to be measured is sealed in the metal bomb under about 20 atm pressure of pure oxygen. By means of a fusible wire and electrical circuit the material is ignited. The rise in temperature of the water (and bomb) is carefully measured with a precision thermometer. The quantity of water is large enough that the rise in temperature is restricted to a few degrees. Essentially the heat effect measured is that at *constant temperature and volume*. From our previous studies, we may immediately say that this quantity corresponds to a *change in internal energy* for the reaction.

We must now determine how the enthalpy change is calculated from the data obtained in the Parr bomb. From the definition of enthalpy,

$$H = U + PV$$

we may write the equation for a change,

$$\Delta H = \Delta U + \Delta (PV)$$

From the measured quantity of heat in the Parr bomb we know ΔU. The only problem remaining is to find $\Delta (PV)$. Since the volume of the bomb is constant, this is equivalent to $V \Delta P$. Suppose that we have present both before and after reaction some gas, liquid, and solid constituents. If it is assumed that the temperature remains constant (the variation in absolute temperature is rarely more than 1 or 2%), the value of $V \Delta P$ can be very closely approximated by $RT \Delta N$, where ΔN is the change in *gaseous* moles present. The effect of having a liquid and/or a solid present in the bomb is to displace some of the gas and to change the pressure, and thus the term $V \Delta P$, slightly. The liquid and/or solid present will rarely fill more than 1% of the bomb and can be neglected. The principles are illustrated by this example:

Example 4-27. A constant-volume bomb weighing 8000 g is made of a metal with a heat capacity of 0.3 cal/(g)(C°). Its inside volume is 1 liter. It is surrounded by 2000 g of water in a container insulated from the outside. Two grams of graphite of specific gravity 2.25 is placed in the bomb. The standard heat of combustion (enthalpy change) is 7838 cal/g. The initial pressure of pure oxygen in the bomb is 25 atm, and the temperature is 25°C.

a. Using the simplest possible equations, calculate the constant-volume heat of combustion and the rise in temperature of the bomb and water.

b. Refine the calculation, taking into account the volume of the graphite and the heat capacity of the bomb contents, and determine an approximate error in the method used in part *a*.

Solution

a. The reaction is

$$\mathrm{C(graphite)} + \mathrm{O_2}(g) = \mathrm{CO_2}(g)$$

The change in *gaseous* moles is zero.

Therefore, $$\Delta U = \Delta H - RT\,\Delta N = \Delta H = \frac{7838 \text{ cal}}{\text{g}}$$

The heat released by the reaction is thus

$$Q = (2 \text{ g})\left(\frac{7838 \text{ cal}}{\text{g}}\right) = 15{,}676 \text{ cal}$$

The total heat capacity of the bomb and water is

$$(2000 \text{ g})\left(\frac{1 \text{ cal}}{(\text{g})(\text{C°})}\right) + (8000 \text{ g})\left(\frac{0.3 \text{ cal}}{(\text{g})(\text{C°})}\right) = \frac{4400 \text{ cal}}{\text{C°}}$$

The temperature rise is

$$\frac{15{,}656 \text{ cal}}{4400 \text{ cal/C°}} = 3.56 \text{ C°}$$

b. We can make a more nearly rigorous calculation by considering the volume of the carbon and the heat capacity of the bomb contents. Some approximations are still inherent in the calculation. These include the neglecting of radiation losses and corrections for deviations from perfect-gas behavior. Both are beyond the scope of this text.

We shall start the calculation with the statement

$$\Delta E = 0$$

where E refers to the total energy of the system, including the bomb and water.

Neglecting kinetic, potential, and miscellaneous energy differences,

$$\Delta U = 0$$

where U = internal energy of the bomb, water, and bomb contents. We need to consider each item separately.

Item	Before reaction			After reaction		
	g	T°K	U	g	T°K	U
Bomb	8000	298	U_{B_1}	8000	T_2	U_{B_2}
Water	2000	298	U_{W_1}	2000	T_2	U_{W_2}
Graphite	2	298	U_{C_1}	0		
Oxygen	$32n_{O_2}$	298	$U_{O_{2(1)}}$	$32(n_{O_2} - 1/6)$	T_2	$U_{O_{2(2)}}$
CO_2	0	...	....	$44(1/6)$	T_2	U_{CO_2}

$$\Delta U_B = (8000)(\bar{C}_v)(T_2 - 298) = 2400\,\Delta T$$

(For solids, $\bar{C}_v = \bar{C}_p$)

$$\Delta U_W = (2000)(\bar{C}_v)(T_2 - 298) = 2000\,\Delta T$$

To calculate ΔU for the reactants and products, we may separate the oxygen into two portions, one of which reacts and one of which does not.

Molar volume at 25 atm and 298°K is

$$\text{Molar } V = (22.4)(1/25)(298/273) = 0.978l \approx 978 \text{ ml}$$

Volume of oxygen initially present is the bomb volume minus the volume of the carbon:

$$V_{O_2} = 100 - \frac{2}{2.25} = 999.1 \text{ ml}$$

Therefore, $$n_{O_{2(1)}} = 999/978 = 1.020 \text{ gmole}$$

Oxygen used $= 2/12 = 0.167$ gmole.

$$n_{O_{2(2)}} = 1.020 - 0.167 = 0.853 \text{ gmole}$$

Therefore, for the oxygen which does not react,

$$\Delta U_{O_2} = n_{O_{2(2)}} \bar{C}_{v_{O_2}} \Delta T$$

The equation may not seem immediately apparent. Visualize it this way: Part of the oxygen which reacts is replaced by CO_2. Assume that it does not mix with the oxygen which does not react. If perfect gases are assumed, the volume of the unreacted oxygen remains constant, except for a slight expansion factor of 1000/999.1, caused by the disappearance of the carbon. Thus we may properly use the $\bar{C}_v$ term. Now, if the unreacted oxygen and product CO_2 mix, owing to the nature of perfect gases the energy changes for changing partial pressure and mixing at constant temperature are zero. Our equation is thus correct without modification.

Now consider the energy change for the reaction. The actual reaction is

$$\tfrac{1}{6}\mathrm{C(graphite,\ 25\ atm,\ 298°K)} + \tfrac{1}{6}\mathrm{O_2}(g,\ 25\ \mathrm{atm},\ 298°\mathrm{K}) + 0.853\mathrm{O_2}(g,\ p_2,\ T_2) = \tfrac{1}{6}\mathrm{CO_2}(g,\ \mathrm{mixed\ with}\ 0.853\mathrm{O_2},\ p_2,\ T_2)$$

It is best to break this into steps for which we can evaluate energy changes. Working on a molar basis and omitting the terms "graphite" and g,

(1) $\mathrm{C}(25\ \mathrm{atm}, 298°\mathrm{K}) = \mathrm{C}(1\ \mathrm{atm}, 298°\mathrm{K})$

(2) $\mathrm{O_2}(25\ \mathrm{atm}, 298°\mathrm{K}) = \mathrm{O_2}(1\ \mathrm{atm}, 298°\mathrm{K})$

(3) $\mathrm{C}(1\ \mathrm{atm}, 298°\mathrm{K}) + \mathrm{O_2}(1\ \mathrm{atm}, 298°\mathrm{K}) = \mathrm{CO_2}(1\ \mathrm{atm}, 298°\mathrm{K})$

(4) $\mathrm{CO_2}(1\ \mathrm{atm}, 298°\mathrm{K}) = \mathrm{CO_2}(p_2, 298°\mathrm{K})$

(5) $\mathrm{CO_2}(p_2, 298°\mathrm{K}) = \mathrm{CO_2}(p_2, T_2)$

(6) $\mathrm{CO_2}(p_2, T_2) + (6)(0.853)\mathrm{O_2}(p_2, T_2) = \mathrm{CO_2}[\mathrm{mixed\ with}\ (6)(0.853)\mathrm{O_2}, (p_2, T_2)]$

These six equations add up to the actual reaction. We may therefore calculate the actual energy change by adding energy changes for these reactions:

(1) $\Delta U \approx 0$ (U of a solid is practically independent of pressure)

(2) $\Delta U = 0$ (perfect gas, isothermal change)

(3) $\Delta U = \Delta H - \Delta(PV)$ (standard conditions)

$\Delta H = -94{,}052$ cal

$\Delta(PV) = RT\,\Delta N = 0$

(4) $\Delta U = 0$ (same reason as 2)

(5) $\Delta U = (n_{\mathrm{CO_2}})(\bar{C}_{v_{\mathrm{CO_2}}})\Delta T$ (perfect gas; ΔU is $\int C_v\,dT$ regardless of process)

(6) $\Delta U = 0$ (explained previously)

Therefore, for the reaction (returning to a basis of $\frac{1}{6}$ mole)

$$\Delta U = \tfrac{1}{6}(-94{,}052) + (1)(\bar{C}_{v_{\mathrm{CO_2}}}\Delta T)$$

Since the over-all ΔU is zero,

$$2400\,\Delta T + 2000\,\Delta T + (0.853)(\bar{C}_{v_{\mathrm{CO_2}}})\,\Delta T - \frac{94{,}052}{6} + (0.167)(\bar{C}_{v_{\mathrm{CO_2}}})\,\Delta T = 0$$

From the tables, using $\bar{C}_v = \bar{C}_p - R$ for perfect gases,

$$\bar{C}_{v_{\mathrm{O_2}}} = 5.0 \qquad \bar{C}_{v_{\mathrm{CO_2}}} = \frac{6.8\ \mathrm{cal}}{(\mathrm{gmole})(\mathrm{C°})}$$

Thus $(4400 + 4.26 + 1.13)\,\Delta T = 15{,}676$ cal

Therefore, $\Delta T = 3.55$ C°

From this example it appears that the error made in neglecting the solid volume and heat capacity of bomb contents is less than small errors

which accumulate because of the use of a slide rule. We may therefore use the simplest approach in determining heats (enthalpies) of combustion from internal-energy values:

$$-\Delta U_c = Q = [(WC_p)_{\text{bomb}} + (WC_p)_{H_2O}]\,\Delta T \tag{4-42}$$

and

$$\Delta H_c = \Delta U_c + RT\,\Delta N \tag{4-43}$$

where ΔN refers to *gaseous* moles.

The term WC_p of the bomb is often called the "water equivalent" of the bomb. Since water has a specific heat of unity, the product WC_p of the bomb represents a heat capacity of that many grams of water. In the example, the water equivalent of the bomb was 2400 g; the bomb and water together had a total water equivalent of 4400 g, or a total heat capacity of 4400 cal/C°.

The example did not bring out one complexity which can arise with compounds containing hydrogen. As we have seen, there is a vast difference between net and gross heating values of some substances, and care must be exercised to avoid errors. Consider this example:

Example 4-28. Two grams of liquid benzene is placed in a Parr bomb under 25 atm oxygen pressure at 25°C. The water equivalent of the bomb and surrounding water is 4400. Determine the rise in temperature of the bomb and water, assuming that

a. All water formed is condensed.

b. Part of the water formed is condensed.

Solution

a. The standard heat of combustion (enthalpy change) is −780,980 cal/gmole for the reaction.

$$C_6H_6(l) + \frac{15O_2}{2}(g) = 6CO_2(g) + 3H_2O(l)$$

when all components are at 1 atm and 25°C.

We have already shown that we may neglect effects of changes in pressure and mixing on enthalpy and internal-energy changes.

$$\Delta U = \Delta H - RT\,\Delta N$$

$$\Delta N = 6 - 15/2 = -3/2 \qquad \text{(gaseous moles!)}$$

Therefore, $\Delta U = -780{,}980 - (1.99)(298)\left(-\frac{3}{2}\right) = -\frac{780{,}090 \text{ cal}}{\text{gmole}}$

In this problem

$$Q = \left(\frac{780{,}090 \text{ cal}}{\text{gmole}}\right)\left(\frac{2}{78} \text{ gmole}\right) = 20{,}000 \text{ cal}$$

and

$$\Delta T = \frac{20{,}000 \text{ cal}}{4400 \text{ cal/C°}} = 4.55 \text{ C°}$$

b. The final temperature is about 29.55°C. At this temperature the

vapor pressure of water is 31.1 mm Hg. We may assume that the gases inside the bomb are saturated with water vapor at this pressure. The moles of vapor present are

$$\frac{1 \text{ liter}}{(22.4 \text{ liters/gmole})(303.55/273)(760/31.1)} = \frac{1}{608} = 0.00165 \text{ gmole}$$

The water formed is

$$\left(\frac{2}{78} \text{ mole benzene}\right)\left(\frac{3 \text{ mole } H_2O}{\text{mole benzene}}\right) = 0.077 \text{ gmole}$$

Therefore there is sufficient water to saturate the gas.

To find the effect of leaving some of the water in the vapor form, assume that the reaction first proceeds to give all water in the liquid form. $Q = 20{,}000$ cal for this.

Now subtract from this the heat used to vaporize the water. We may use the *enthalpy change of vaporization*, since the water may be assumed to *vaporize against its own constant vapor pressure.*

At 29.6°C, $\Delta H_{vap} = 10{,}450$ cal/gmole.

$$\left(\frac{10{,}450 \text{ cal}}{\text{gmole}}\right)(0.00165 \text{ gmole}) = 17.2 \text{ cal}$$

$$Q = 20{,}000 - 17.2 = 19{,}983 \text{ cal}$$

$$\Delta T = \frac{19{,}983}{4400} = 4.54 \text{ C°}$$

In this problem the effect of having some of the water in the vapor form did not change the answer. However, a larger error might appear when smaller samples with less hydrogen per mole are used. It is not necessary to speculate about this, however, as there is a very simple and practical way to avoid these difficulties experimentally. When the Parr bomb is used, a small amount of liquid water is placed in the bottom of the container, so that the oxygen initially present is saturated with water. In this way, all the water formed is condensed, and a higher or gross heating value is obtained.

Use of the Thermodynamic Path. Our discussion of thermochemistry up to this point has dealt primarily with heat effects at standard conditions, since these conditions form the basis for experimental work and the interpretation of laboratory data. Practical industrial cases demand, however, that we consider cases where standard conditions are not maintained. A practical question might be "How much heat must be added or removed per unit time if the reactants enter the system at a certain temperature, pressure, composition, and rate, and the products are removed at a certain (different) temperature, pressure, and composition (and the same rate, due to steady state)?"

To solve such problems we have at our disposal the concept of the thermodynamic path. Consider the case suggested in the question above. If we have a steady-state flow system, neglecting kinetic, potential, and miscellaneous energy effects, and assuming no work-producing device within the system, we know that $Q = \Delta H$. We also know that we may break down any process into a series of steps, both physical and chemical, for which we can evaluate enthalpy changes. If these steps add up to the desired process, then the enthalpy changes for the steps add up to the enthalpy change for the process. Thus, assume in the above case that the initial conditions, P_1 and T_1, and the final conditions, P_2 and T_2, are above standard conditions. We might proceed as follows:

1. Reduce the pressure from P_1 to P_s (standard conditions).
2. Reduce the temperature from T_1 to T_s.
3. Separate the reactants into pure materials (if necessary).
4. Carry out the reaction at standard conditions.
5. Mix the products (if necessary) at standard conditions.
6. Heat the products from T_s to T_2.
7. Compress the products from P_s to P_2.

These steps, when added, give the desired process. We may therefore add the enthalpy changes to get the change for the over-all reaction.

In this text, unless very specific instructions to the contrary are given, we shall assume the enthalpy changes for steps 1 and 7 to be zero. It is true that pressure has no effect on the enthalpy of perfect gases at constant temperature. The pressure effects on enthalpies of liquids and solids are small and may justifiably be neglected. It is only in the case of nonideal gases that there is an appreciable effect of pressure on enthalpy. Since the evaluation of this effect requires more thermodynamics than we are able to present at this time, we must defer a study of it. You should recognize that it does exist, just as you know that most gases deviate from the perfect-gas law.

We may group steps 3, 4, and 5 together, under the single term "reaction," if we understand what we mean by this term. For example, in calculating the heat necessary to concentrate a sodium hydroxide solution from concentration z_1 (weight fraction) to z_2, we would consider separating the water and sodium hydroxide into pure components (step 3), evaporating the necessary water (step 4), and recombining the sodium hydroxide and remaining water (step 5). Thus we may rewrite the process in three steps:

1. Reduce the temperature from T_1 to T_s.
2. Carry out the process, including dilution and concentration.
3. Heat the products from T_s to T_2.

Again we emphasize the approximations involved. Also, it is customary

to think of reactions as being carried out at a higher temperature than standard, and it is easy to say "reduce the temperature of the reactants and heat the products"; the equations, however, are valid for cases where the reaction temperature is below the standard value.

With the process reduced to three steps, we may write an equation for each of these steps:

$$\Delta H_1 = \int_{T_1}^{T_s} N_R C_{p_{m(R)}}\, dT = N_R \bar{C}_{p_{m(R)}}(T_s - T_1) \tag{4-44}$$

In the case of gases, since we are concerned with perfect gases only,

$$\Delta H_1 = \sum_{i=R} n_i \int_{T_1}^{T_s} C_{p_i}\, dT = \sum_{i=R} n_i \bar{C}_{p_i}(T_s - T_1) \tag{4-45}$$

$$\Delta H_2 = \Delta H_r \tag{4-46}$$

where ΔH_r is the standard heat of reaction, including dilution effects.

$$\Delta H_3 = \int_{T_s}^{T_2} N_P C_{p_{m(p)}}\, dT = N_P \bar{C}_{p_{m(P)}}(T_2 - T_s) \tag{4-47}$$

or, for perfect gases,

$$\Delta H_3 = \sum_{i=P} n_i \int_{T_s}^{T_2} C_{p_i}\, dT = \sum_{i=P} n_i \bar{C}_p (T_2 - T_s) \tag{4-48}$$

In these equations the subscripts R and P have been added to mean "reactants" and "products," respectively. As we have noted from our work on gases, we avoid integration of polynomial equations for heat capacities and use mean values where possible. Thus, the most convenient forms of the equations for H_1 and H_3 are those using the mean heat capacities. For the usual case, then,

$$\Delta H = N_R \bar{C}_{p_{m(R)}}(T_s - T_1) + \Delta H_r + N_P \bar{C}_{p_{m(P)}}(T_2 - T_s) \tag{4-49}$$

In many cases the solution lends itself readily to tabular form.

Example 4-29. The standard heat of combustion of graphite is $-94{,}052$ cal/gmole. What is the "standard" heat of combustion at 1000°F?

Solution. Occasionally the word "standard" is applied to *any* heat of reaction where the pressure and temperature of reactants and products are the same. To avoid confusion, we do not recommend the use of the term and would prefer to reword the question, "What is the heat of combustion of graphite at 1 atm when both reactants and products are at 1000°F?"

The desired equation is

$$\text{C(graphite, 1 atm, 1000°F)} + \text{O}_2(g,\ 1\ \text{atm},\ 1000°\text{F}) = \text{CO}_2(g,\ 1\ \text{atm},\ 1000°\text{F})$$

Since the heat of combustion is known at 25°C, the following steps must be taken:

1. Cool the carbon and oxygen to 25°C (77°F).

$$\Delta H_1 = \int_{1000}^{77} C_{p_C}\,dt + \int_{1000}^{77} C_{p_{O_2}}\,dt$$

2. Carry out the reaction at 25°C.

$$\Delta H_2 = \frac{(-94{,}052)(1.8)\ \text{Btu}}{\text{lbmole}}$$

3. Heat CO_2 to 1000°F.

$$\Delta H_3 = \int_{77}^{1000} C_{p_{CO_2}}\,dt$$

Using mean heat capacities,

$$\Delta H = (\bar{C}_{p_C} + \bar{C}_{p_{O_2}})(77 - 1000) - 169{,}294 + (\bar{C}_{p_{CO_2}})(1000 - 77)$$

$$\Delta H = (3.7 + 7.6)(-923) - 169{,}294 + (10.8)(923)$$

Therefore, $$\Delta H = \frac{-169{,}762\ \text{Btu}}{\text{lbmole}} \approx \frac{-94{,}312\ \text{cal}}{\text{gmole}}$$

A study of this example shows that a simpler equation may be used for the cases where the temperature of reactants and products is the same. The first and third enthalpy changes involve integration between the same limits (but in opposite directions).

They may be combined to give

$$\Delta H_1 + \Delta H_3 = (\Sigma(nC_p)_P - \Sigma(nC_p)_R)(t - t_s) \qquad (4\text{-}50)$$

where t = reaction temperature and t_s = base temperature.

If mean heat capacities are not available and cannot be estimated with sufficient accuracy, it may be necessary to perform the actual integrations. In this case, again, it is possible to simplify the relationships somewhat for cases where the reactant temperature equals the product temperature. It is also desirable at times to derive an equation for heat of reaction as a function of temperature, i.e., to leave the temperature as a variable in the final equation.

Example 4-30

a. Derive an equation for the heat of reaction when the standard value is known and all the heat capacities are known as functions of temperature. Assume in this case the special form

$$C_p = a + bT + \frac{c}{T^2} \qquad (4\text{-}51)$$

b. Determine the constants in the equation for the case of combustion of graphite.

Solution

a. For a general case, assume that the reactants are W and X and the products Y and Z.

Let w = mole of W, etc., and so the equation is

$$wW + xX = yY + zZ$$

where all the materials are at the same P and T. Again taking a three-step process,

$$\Delta H_1 = w \int_T^{T_s} C_{pw}\, dT + x \int_T^{T_s} C_{px}\, dT$$
$$\Delta H_2 = \Delta H_{R,s}$$
$$\Delta H_3 = y \int_{T_s}^{T} C_{pY}\, dT + z \int_{T_s}^{T} C_{pz}\, dT$$

The four C_p values are of the same form, and the integrals may be grouped in this manner:

$$\Delta H_1 + \Delta H_3 = (ya_Y + za_Z - wa_W - xa_X) \int_{T_s}^{T} dT + (yb_Y + zb_Z - wb_W - xb_X) \int_{T_s}^{T} T\, dT + (yc_Y + zc_Z - wc_W - xc_X) \int_{T_s}^{T} \frac{dT}{T^2}$$

Defining

$$\Delta a = ya_Y + za_Z - wa_W - xa_X \tag{4-52}$$

and similar expressions for Δb and Δc,

$$\Delta H_1 + \Delta H_3 = (\Delta a)(T - T_s) + \left(\frac{\Delta b}{2}\right)(T^2 - T_s^2) - (\Delta c)\left(\frac{1}{T} - \frac{1}{T_s}\right) \tag{4-53}$$

b. From the Chemical Engineers' Handbook* we obtain these expressions for C_p:

C:	$2.673 + 0.002617T - 116{,}900/T^2$
O_2:	$8.27 + 0.000258T - 187{,}700/T^2$
CO_2:	$10.34 + 0.00274T - 195{,}500/T^2$

where T = °K.

In this case

$$\Delta a = a_{CO_2} - a_C - a_{O_2} = 10.34 - 2.67 - 8.27 = -0.60$$

Similarly,

$$\Delta b = -0.00014$$

and

$$\Delta c = -109{,}100$$

Thus, a general expression for the heat of combustion of carbon

* John H. Perry (ed.), 3d ed., McGraw-Hill Book Company, Inc., New York, 1950.

(graphite) is

$$\Delta H = -94{,}052 - (0.60)(T - 298) - \frac{0.00014(T^2 - 298^2)}{2} + (109{,}100)\left(\frac{1}{T} - \frac{1}{298}\right)$$

For the case of the previous example, when $t = 1000°F$, $T = 811°K$. Substituting this in the equation, we obtain

$$\Delta H = \frac{-94{,}632 \text{ cal}}{\text{gmole}}$$

One precaution is necessary when working with power-series expressions for C_p. These are empirically fitted equations and are valid over a restricted temperature range. Thus, in Example 4-30, the expression for C_p of carbon was valid between 273 and 1373°K; that for CO_2, between 273 and 2500; and that for oxygen, between 300 and 5000°K. We should therefore expect our final expression to be valid from 300°K up to about 1373°K.

These examples illustrate the usefulness of the thermodynamic path in the solution of heat-balance problems. The procedure is valid (and of the greatest value) for determining heat loads in equipment, i.e., the heat to be added or removed during the course of a reaction. In many cases the equipment is isothermal. In such cases the reactants and products are at the same temperature, and heats of reaction at the temperature in question are used. In more cases, however, the reactants and products are at different temperatures. This does not in any way invalidate the method. It may, however, make the calculations somewhat longer.

Example 4-31. Pure CO is mixed with 100% excess air and completely burned at constant pressure. The reactants are originally at 200°F. Determine the heat added or removed if the product temperature is 200, 500, 1000, 1500, 2000, and 3000°F.

Solution

Basis: 1 lbmole CO

$$CO + \tfrac{1}{2}O_2 = CO_2$$

For 100% excess air, oxygen added is 1 mole, and nitrogen supplied in the air is 3.76 mole. Tabulating reactants and products:

Component	Mole in reactants	Mole in products
CO	1.00	0
CO_2	0	1.00
O_2	1.00	0.50
N_2	3.76	3.76

Assuming a base temperature of 25°C (77°F) and using mean heat capacities,

$$\Delta H = H_P - H_R$$

Therefore, $\Delta H = \Sigma(n\bar{C}_p)_R(77 - 200) + \Delta H_{r(25°C)} + \Sigma(n\bar{C}_p)_P(t_2 - 77)$

and $$Q = \Delta H$$

$$\Delta H_r = -\frac{121{,}745 \text{ Btu}}{\text{lbmole}} \text{ at } 25°\text{C}$$

For the reactants, $\Sigma(n\bar{C}_p)_R$ is obtained in this table:

Component	n	$\bar{C}_p$	$n\bar{C}_p$
CO	1.00	6.95	6.95
O_2	1.00	7.10	7.10
N_2	3.76	6.95	26.13
			40.18

Therefore $$\Sigma(n\bar{C}_p)_R(77 - 200) = -4942 \text{ Btu}$$

and $$\Delta H = Q = -126{,}687 + \Sigma(n\bar{C}_p)_P(t - 77)$$

Setting this up in tabular form:

Component	n	$t = 200$		$t = 500$		$t = 1000$		$t = 1500$		$t = 2000$		$t = 3000$	
		$\bar{C}_p$	$n\bar{C}_p$	$\bar{C}_p$	$n\bar{C}_p$	$\bar{C}_p$	$n\bar{C}_p$	$\bar{C}_p$	$n\bar{C}_p$	$\bar{C}_p$	$n\bar{C}_p$	$\bar{C}_p$	$n\bar{C}_p$
CO_2	1.00	9.15	9.15	9.90	9.90	10.85	10.85	11.50	11.50	12.05	12.05	12.75	12.75
O_2	0.50	7.10	3.55	7.25	3.63	7.55	3.78	7.80	3.90	8.00	4.00	8.30	4.15
N_2	3.76	6.95	26.13	7.00	26.32	7.15	26.88	7.35	27.64	7.55	28.39	7.85	29.42
$\Sigma(n\bar{C}_p)_P$			38.83		39.85		41.51		43.04		44.44		46.32
$\Sigma(n\bar{C}_p)_P(t - 77)$			4,776		16,857		38,314		61,246		85,458		135,810
$Q = \Delta H$			−121,911		−109,830		−88,373		−65,441		−41,229		+9,123

Adiabatic-reaction Temperature. In the tabulation, Q represents heat added. If this quantity is plotted vs. temperature, the temperature at which no heat is added is about 2810°F. Such a condition might be expected in an insulated piece of equipment. Processes which are carried out in such a manner that there is no heat interchange with the surroundings are called *adiabatic*. We have previously defined them mathematically by the statement that $Q' = 0$.

The adiabatic case is a very important one. Most industrial equipment is run under conditions where the variables can be controlled. Typical examples are constant temperature, constant pressure, or constant volume. The other common case is the adiabatic. In this case one other variable, most commonly pressure, may also be controlled.

The adiabatic case arises in insulated equipment and also in cases where the chemical reaction (or physical process) is so rapid that heat transfer with the surroundings is negligible.

The most common case of an adiabatic reaction where the equipment may not be insulated is the combustion reaction. In Example 4-31 the temperature 2810°F is the *theoretical flame temperature*. Such temperatures are usually not attained in actual flames, because of radiant heat loss, but they represent the upper limit of temperature when there are no heat losses.

Example 4-31 shows one method by which a theoretical flame temperature may be calculated. The calculation is sometimes done by trial and error as illustrated below:

Example 4-32. Calculate the theoretical flame temperature for CO burned at constant pressure with 100% excess air, when the reactants enter at 200°F.

Solution. From Example 4-31, we may write

$$\Delta H = 0 = -126{,}687 + \Sigma(n\bar{C}_p)_P(t - 77)$$

Therefore,

$$t = 77 + \frac{126{,}687}{\bar{C}_{p_{CO_2}} + 0.5\bar{C}_{p_{O_2}} + 3.76\bar{C}_{p_{N_2}}}$$

The procedure is to assume t, substitute values of $\bar{C}_p$'s for this temperature, and calculate t. From the calculated value a new t is assumed, and the procedure repeated until the calculated and assumed values agree.

Component	n	t = 3000		t = 2800		t = 2830	
		$\bar{C}_p$	$n\bar{C}_p$	$\bar{C}_p$	$n\bar{C}_p$	$\bar{C}_p$	$n\bar{C}_p$
CO_2	1	12.75	12.75	12.65	12.65	12.65	12.65
O_2	0.5	8.30	4.15	8.20	4.10	8.25	4.13
N_2	3.76	7.85	29.42	7.80	29.33	7.80	29.33
$\Sigma(n\bar{C}_p)$			46.32		46.08		46.11
$\frac{126{,}687}{\Sigma(n\bar{C}_p)}$			2735		2749		2747
t (calculated)			2812		2826		2824

The last trial in the calculation is probably not justified. Most heat-capacity data are reported on plots which cannot be read to the precision which allows the calculation to four significant figures. Furthermore, use of the slide rule does not give this precision. From the first and second trials it is evident that a slight change in the estimated temperature would not change the final calculated value significantly. The flame temperature is about 2820°F, which compares favorably with the value of 2810 estimated from the plot of values in Example 4-31.

The principles illustrated in the example are applicable to all adiabatic-reaction problems. The method used is purely an application of the thermodynamic path. In all cases the ΔH (assuming a constant-pressure process) is equal to the heat transferred with the surroundings. Setting this equal to zero specified the adiabatic process.

Example 4-33. One grammole of $CaCl_2$ is added to 10 gmole of water at 25°C in an insulated container at constant pressure. How hot does the mixture become?

Solution

Basis: 1 gmole $CaCl_2$ + 10 gmole H_2O. From a plot of integral heat of solution of $CaCl_2$ in water,

$$\Delta H_r = -15{,}500 \text{ cal}$$

The weight of solution is

$$\begin{aligned}(1)(40 + 71) &= 111 \text{ g } CaCl_2\\ (10)(18) &= \underline{180 \text{ g } H_2O}\\ &\quad 291 \text{ g total}\end{aligned}$$

The approximate specific heat (actually a point value at 20°C) is 0.60.

$$\Delta t = \frac{\Delta H_r}{W\bar{C}_p} = \frac{15{,}500}{(291)(0.6)} = 88.5 \text{ C°}$$

Therefore, the final temperature is

$$\begin{aligned}&88.5\\ &\underline{+25.0}\\ &113.5°\text{C}\end{aligned}$$

(if the solution does not boil below this temperature).

We may also obtain flame (or reaction) temperatures at constant volume. In this case, from the thermodynamic analysis of the constant-volume-batch process, $\Delta U = 0$. Thus,

$$\Delta U = 0 = \Sigma(n\bar{C}_v)_R(t_b - t_1) + \Delta U_r + \Sigma(n\bar{C}_v)_P(t_2 - t_b) \qquad (4\text{-}54)$$

where t_1 = temperature of reactants

t_b = base temperature

t_2 = temperature of products = reaction temperature

In the case of reactions with solids and liquids, ΔU_r and ΔH_r are approximately equal. Furthermore, C_p and C_v values are about the same. Thus, in general, we may say that the adiabatic-reaction temperatures in such systems are about the same for constant volume and constant pressure. In the case of gases, however, there may be large differences. The ΔU_r and ΔH_r often do not vary greatly, but the C_v values are always considerably lower than the C_p values. When no data are available for C_v values, assume $C_v = C_p - R$.

Example 4-34. What is the theoretical flame temperature of CO burned with 100% excess air at constant volume? The initial temperature is 200°F.

Solution

Basis: 1 lbmole CO. All stoichiometric quantities are the same as in Examples 4-31 and 4-32.

$$\Delta U = 0 = \Sigma(n\bar{C}_v)_R(77 - 200) + \Delta U_{r(25°C)} + \Sigma(n\bar{C}_v)_P(t_2 - 77)$$

$$\Delta U_r = \Delta H_r - \Delta(PV) = \Delta H_r - RT\,\Delta N = -121{,}745 - (1.987)(537)(-0.5) = \frac{-121{,}211 \text{ Btu}}{\text{lbmole CO}}$$

For the reactants, $\Sigma(n\bar{C}_v)_R$ is obtained in this table:

Component	n	$\bar{C}_p$	$\bar{C}_v$	$n\bar{C}_v$
CO	1.00	6.95	4.96	4.96
O_2	1.00	7.10	5.11	5.11
N_2	3.76	6.95	4.96	18.65
				28.72

$$(28.72)(77 - 200) = -3533 \text{ Btu}$$

Therefore, $\Delta U = 0 = -3533 - 121{,}211 + \Sigma(n\bar{C}_v)_P(t_2 - 77)$

and

$$t_2 = 77 + \frac{124{,}744}{\Sigma(n\bar{C}_v)_P}$$

Component	n	$t = 4000$			$t = 3500$		
		$\bar{C}_p$	$\bar{C}_v$	$n\bar{C}_v$	$\bar{C}_p$	$\bar{C}_v$	$n\bar{C}_v$
CO_2	1	13.25	11.25	11.25	13.00	11.00	11.00
O_2	0.5	8.50	6.50	3.25	8.40	6.40	3.20
N_2	3.76	8.05	6.05	22.75	7.95	5.95	22.37
$\Sigma n\bar{C}_v$				37.25			36.57
$\frac{124{,}744}{\Sigma n\bar{C}_v}$		3348			3411		
t (calculated)		3425			3488		

The estimated constant-volume flame temperature is thus about 3490°F.

We have attempted in this chapter to introduce the background material for "heat balances" in a fairly rigorous style. More could have been done, but to do so would not only cover too much of later courses

but would also preclude your going further in this course in the usual time allotted.

In making a heat balance we may use the equation "input-output = accumulation" just as we do in material balances. We must sometimes look more carefully to find all the input and output energy. Even in the restricted cases we have covered we must consider chemical energy, sensible heat, and latent heat. While we have excluded work, potential energy, kinetic energy, and other miscellaneous forms of energy from our final equations, we have nevertheless made every effort to emphasize the restrictions thereby placed on our working equations.

These basic points have been made during the discussion:

1. For a constant-volume batch system

$$Q = \Delta U$$

2. For a constant-pressure batch system

$$Q = \Delta H$$

3. For a steady-state flow system

$$Q' = \Delta H$$

4. $C_p = \left(\frac{\partial H}{\partial T}\right)_p = \frac{dQ}{dT}$ at constant pressure

5. $C_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{dQ}{dT}$ at constant volume

6. A mean heat capacity is defined by

$$\bar{C} = \frac{\int c\, dT}{\int dT}$$

7. For perfect gases, C_p and C_v are functions of temperature only, and

$$C_p = C_v + R$$

8. For phase changes at constant pressure

$$Q = \Delta H$$

where ΔH may be heat of fusion or vaporization.

9. The change in a property, such as U or H, is independent of the path by which the change is calculated.

10. The equations such as $Q = \Delta U$, $Q = \Delta H$, and $Q' = \Delta H$ are equally applicable to chemical and physical changes.

11. In thermochemical equations sufficient descriptive material must be included to define the states of the materials completely.

12. All the enthalpy effects, such as heats of dilution, combustion, reaction, and formation, may be considered as heats of reaction.

13. If a series of thermochemical equations is added to obtain a desired equation, the enthalpy change of this desired reaction is obtained by adding the enthalpy changes of the series of reactions.

14. Heats of mixing of perfect gases are zero. Thus we may use mixed heat capacities defined as

$$C_{p_m} = \Sigma y_i C_{p_i}$$

15. Constant-pressure heats of reaction (enthalpies) may be calculated from constant-volume calorimetric measurements by

$$\Delta H = \Delta U + RT\,\Delta N$$

where ΔN = change in number of gaseous moles.

16. Adiabatic reactions or processes are defined by $Q' = 0$. Specific examples of the use of this concept are the theoretical flame temperature and the adiabatic-reaction temperature.

PROBLEMS

4-1. Make the following conversions:

a. A rate of heat flow of 5000 Btu/(hr)(ft²) to cal/(sec)(cm²)

b. A heat capacity of 3 Btu/(lb)(F°) to cal/(g)(C°)

c. A thermal conductivity of 200 Btu/(hr)(ft)(F°) to cal/(sec)(cm)(C°)

4-2. The heat capacity in Btu/(lbmole)(F°) of CO_2 at atmospheric pressure is given approximately by

$$C_p = 9.00 + 2.71 \times 10^{-3}t - 0.256 \times 10^{-6}t^2$$

where t = °F.

a. Working in each case from this equation, find equations for C_p as functions of temperature for the following sets of units:

	C_p	Temperatures
(1)	Btu/(lbmole)(R°)	°R
(2)	cal/(gmole)(C°)	°C
(3)	cal/(gmole)(C°)	°K
(4)	Btu/(lbmole)(C°)	°C
(5)	Chu/(lbmole)(C°)	°C
(6)	kcal/(kgmole)(C°)	°C
(7)	cal/(g)(C°)	°C
(8)	Btu/(lb)(F°)	°F

b. Choosing a convenient temperature, say 0°C, compare numerical values of C_p from the above equations. Indicate which values should be numerically the same.

4-3. Numerous equations have been proposed to fit curves of C_p vs. temperature. One form, in descending power series as opposed to the ascending series of the usual polynomial form, is

$$C_p = a + \frac{b}{T} + \frac{c}{T^2} + \cdots$$

a. For the three-term form, calculate the amount of heat necessary to heat a material from T_1 to T_2.

b. Determine the average heat capacity between T_1 and T_2 for the two-term form.

c. Determine the average heat capacity between T_1 and T_2 for the three-term form.

4-4. When the heat capacity of a substance is a linear function of temperature,

$$C_p = a + bT$$

where T = absolute temperature.

a. Show that the mean heat capacity between two temperatures T_1 and T_2 is the same as the true or point value of the heat capacity at the average temperature $(T_1 + T_2)/2$.

b. Show whether the above statement is true or false when the heat capacity is a linear function of temperature:

$$C_p = a + bt$$

where t is temperature in °F or °C instead of absolute temperature.

4-5. SO_3 has a molal heat capacity of

$$C_p = 8.20 + 10.236 \times 10^{-3}T - 3.156 \times 10^{-6}T^2$$

where C_p = cal/(gmole)(C°) and T = temperature, °K.

a. Calculate the true molal heat capacity at 100°C.

b. Calculate the mean molal heat capacity between 0 and 100°C.

c. How many Btu are needed to heat 100 lb of SO_3 vapor from 0 to 100°C?

4-6. The point and average heat capacities of a substance are

$$C_p = a + bt + ct^2$$

and

$$\bar{C}_p = a' + b't + c't^2$$

Assume these equations are for t in °C and C_p in cal/(gmole)(C°). The $\bar{C}_p$ is based on a temperature t in °C. Show that the same equation is obtained for $\bar{C}_p$ in Btu/(lbmole)(F°) and t in °F by

a. Direct conversion of the equation for $\bar{C}_p$

b. Conversion of the equation for C_p followed by integration

4-7. Example 4-6 in the text asks how much heat is necessary to heat 1 lbmole of CO_2 from 200 to 800°F. The following point values of heat capacity are available:

t,°F	0	200	400	600	800	1000
C_p	9.00	9.53	10.04	10.54	11.01	11.45

Various methods for solving the problem are shown.

a. Solve the three simultaneous equations to find the constants in the equation for C_p as a function of temperature.

b. Perform the graphical integration described in the problem.

c. Perform the numerical integration described, using 100-F° intervals instead of 200-F° intervals.

d. Plot enthalpy vs. temperature, using a base temperature of 500°F, and solve the problem.

4-8. Toluene, C_7H_8, has a heat of vaporization of 86.5 cal/g at 100°C. The C_p of the liquid is 0.44; that of the vapor is 0.32.

a. Calculate the heat of vaporization in cal/gmole at 40°C.

b. Calculate the heat of vaporization in Btu/lbmole at 40°C.

c. Calculate the enthalpy of toluene vapor at 150°C if the enthalpy of the liquid is arbitrarily set at zero at 18°C.

4-9. How much heat would be absorbed or released from the hydrogenation of acetylene to ethane at standard conditions?

$$HC{\equiv}CH + 2H_2 \rightarrow CH_3CH_3$$

a. Use heat-of-combustion data for the calculation.
b. Perform the same calculation using heat-of-formation data.

4-10. When water is added to calcium carbide, the reaction

$$CaC_2 + H_2O \rightarrow CaO + C_2H_2$$

takes place with the evolution of acetylene. What heat effect is associated with this reaction at 25°C?

4-11. *a.* Using heat-of-combustion data, calculate the heat of formation of methyl alcohol in cal/gmole at standard conditions of 1 atm and 25°C.

b. Calculate the heat of formation in Btu/lb.

4-12. The standard heat of combustion of methane, CH_4, is $-212{,}798$ cal gmole when the water formed is in the liquid state. What is it when the water is assumed to remain in the vapor state?

4-13. Given the following standard heats of combustion in cal/gmole:

Benzene (l) to CO_2 and $H_2O(l)$	$-780{,}980$
Benzene (g) to CO_2 and $H_2O(g)$	$-757{,}520$
Hydrogen to $H_2O(l)$	$-\ 68{,}317$
Hydrogen to $H_2O(g)$	$-\ 57{,}798$
Graphite to CO_2	$-\ 94{,}052$

Calculate the following:

a. The heat of combustion for benzene (l) to water (g)
b. The heat of combustion for benzene (g) to water (l)
c. The heat of vaporization of benzene

4-14. Five grammoles of water is added to 5 gmole of 20%m HCl in water at 25°C. How much heat is released or absorbed?

4-15. Which is the cheaper fuel, Pyrofax (pure propane) at \$11/100 lb or natural gas at \$1.25/1000 ft³? The natural gas has a gross heating value of 950 Btu/ft³. Compare net heating values. The natural gas is 67.0% ethane (C_2H_6), 32.3% methane (CH_4), and 0.7% N_2.

4-16. *a.* Calculate ΔH_f (heat of formation) of n-pentane at 25°C and 1 atm from heat-of-combustion data.

b. Calculate ΔU at 25°C for the formation of n-pentane.

4-17. One gram of pentene-1 is burned with oxygen in a constant-volume bomb. The experiment is run at 25°C with a pressure of 2 atm at the start. If the bomb is assumed to have a heat-capacity equivalent to 500 g of water, how much water must be placed around the bomb so that the total rise in temperature is not more than 1.0 C°? Assume that the pentene-1 is a gas at the time of combustion and that all water formed is condensed. State any other assumptions made.

4-18. In an experimental study of the fundamentals of gas producers, pure steam is blown through a bed of glowing carbon. The over-all reactions which occur (although there may be numerous simultaneous side reactions) are

$$C + H_2O(g) \rightarrow CO + H_2 \qquad (A)$$

and

$$C + 2H_2O(g) \rightarrow CO_2 + 2H_2 \qquad (B)$$

In one experiment steam at 1 atm and 1600°F is blown through carbon also at this temperature. Assuming that the heat capacity of carbon is constant at 3 Btu/(lb-mole)(F°), calculate

a. The heat of reaction for (*A*) at 1600°F

b. The heat of reaction for (*B*) at 1600°F

4-19. In the hypothetical reaction

$$A + B \rightarrow C$$

the heat of reaction at 20°C is −10,000 cal/gmole of *C* formed. If the C_p values are

A: $6.0 + 0.05t$
B: $6.5 + 0.20t$
C: $15.0 + 0.60t$

where C_p = cal/(gmole)(C°) and t = °C, at what temperature, in °C, does the reaction change from exothermic to endothermic?

4-20. In an experiment, methane (CH_4) is burned with the theoretical quantity of air for complete combustion. Because of faulty construction and operation of the equipment, the reaction does not proceed to completion; all the carbon which burns, however, goes to CO_2. If the methane and air are originally at 25°C and the total products (including unburned CH_4 and unused O_2) leave at 400°C, what percentage of the methane is burned? Note that the water leaves in the vapor form.

4-21. Dry methane is burned with dry air. Both are at 25°C initially. The flame temperature is 1300°C. If complete combustion is assumed, how much excess air is being used?

4-22. Methane at 25°C and 1 atm pressure is burned with 100% excess air, also originally at 25°C and 1 atm. What is the theoretical flame temperature? (Water produced would be in the vapor state in the flame.) The reaction is carried out at constant pressure.

4-23. Which gas will give the higher maximum theoretical flame temperature when burned in a torch with air, Pyrofax (assumed pure propane, C_3H_8) or acetylene (C_2H_2)?

4-24. One grammole of solid KOH at 25°C is added to 20 gmole of water, also at 25°C. No heat is allowed to escape. Estimate the final temperature of the mixture.

4-25. Plot the theoretical flame temperature in °F vs. per cent excess oxygen from −100% (no oxygen fed) to 500% for the combustion of CO originally at 25°C for these cases:

a. Combustion with pure oxygen at constant pressure (1 atm)

b. Combustion with air at constant pressure

c. Combustion with air at constant volume

Show sample calculations for all cases for 25% *of* theoretical and 500% *excess*. (Parts of some curves may be outside the range of available data and may be omitted. The solution can be simplified by the use of a tabular form.)

4-26. A solution of 10%w NaOH in water is concentrated by evaporation to 50%w. The solution is initially at 90°F. At the end of the process the hot concentrated solution is at 230°F. The water vapor leaves at an average temperature of 212°F. How much heat is supplied per ton of initial mixture?

4-27. The following data are available for the integral heat of solution of NaOH at 25°C:

Mole H_2O/*mole* NaOH	ΔH_{soln}, *cal/gmole* NaOH
0	−0
2	−4,600
4	−8,300
6	−9,900
8	−10,200
10	−10,300
16	−10,300
20	−10,200
50	−10,100

Calculate the number of Btu necessary to concentrate 100 lb of 18.2%w solution NaOH to 52.6%w under a pressure of 1.94 psia. The boiling point of the 52.6% solution at this pressure is about 195°F. Assume both feed and products at this temperature. Show clearly the thermochemical equations used in obtaining the solution.

4-28. The gases entering a sulfur converter contain 2.1%m SO_3, 8.5% SO_2, 9.6% O_2, and 79.8% N_2. Only the reaction

$$SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3$$

takes place. No materials are added or removed except by the single process stream. The outlet gases contain 82.46% N_2. How much heat is evolved per 100 gmole of entering gas, if the reaction takes place isothermally at 450°C?

Chapter 5

UNIT OPERATIONS

Prior to World War I, the chemical industry in the United States was chiefly occupied with the production of "heavy" chemicals. Heavy chemicals are relatively simple inorganic compounds, like lime and sulfuric acid, that are so widely used that they must be produced in tremendous quantities. The production was supervised by men who were called "industrial chemists." These individuals had to have a knowledge of mechanical engineering as well as chemistry because a major part of their consideration was the pumping, heating, cooling, and mixing of process materials. In addition they were concerned with operations such as distillation and filtration which were employed to separate materials and which were not a part of any recognized technology. The advent of World War I forced the development of organic chemical technology and created a demand for more industrial chemists as the United States was freed from dependence on Germany for synthetic organic chemicals.

The effort of the American manufacturers to produce materials cheaply on a large scale required economical utilization of heat and power and led to further investigation of separation processes from the standpoint of equipment design. In 1915, Arthur D. Little and William H. Walker described the concept of "unit" operations in a report to the corporation of the Massachusetts Institute of Technology. They classified industrial processes into operations such as distillation, evaporation, and filtration for which certain recognizable types of equipment were used. This led to a quantitative approach to the operations and to the development of chemical engineering as we know it today. In 1922, the American Institute of Chemical Engineers accepted the following first official definition of chemical engineering:

"Chemical engineering, as distinguished from the aggregate number of subjects comprised in courses of that name, is not a composite of chemistry and mechanical and civil engineering, but itself a branch of engineering, the basis of which is those unit operations which in their proper sequence and coordination constitute a chemical process as conducted on the industrial scale."

The definition accepted by the A.I.Ch.E. at present is as follows:

"Chemical engineering is the application of the principles of the physical sciences together with the principles of economics and human relations to fields that pertain directly to processes and process equipment in which matter is treated to effect a change in state, energy content, or composition."

In the remainder of this chapter, we describe the field of chemical engineering, discuss and classify operations, and finally apply heat and material balances to certain selected unit operations.

CHEMICAL ENGINEERING

The basic objective of chemical engineers is to produce chemical products at a profit. To meet this objective, they must be interested not only in the design, construction, and operation of individual pieces of equipment, but also in the development of entire manufacturing processes. The general scheme of development of a new process involves numerous steps. A new product for which a demand seems apparent is developed by a chemist in most cases. In general, he works with small bench-sized apparatus. The engineering group of a company is given the job of evaluating the possibilities of building a plant to mass-produce this chemical.

After a preliminary evaluation, including market research by the sales division, it may be desirable to carry out pilot-plant studies. These are done in a small plant, producing perhaps 100 lb a day, where studies are made concerning the proper range of temperature, pressure, composition, time, etc., to make the product economically. Other factors such as safety hazards, materials of construction, and waste disposal are also considered here. This work is usually done by chemical engineers.

If the pilot-plant studies seem favorable, full-scale design may be undertaken. Calculations of quantities of materials, energy balances, plant layout, and approximate equipment size are usually done by chemical engineers. Detail design of equipment, controls, electrical wiring, etc., is then usually done by mechanical, electrical, civil, architectural, and other engineers and specialists.

During plant construction numerous members of the engineering department are on hand to check progress and to advise on questionable details.

After the plant is built, the supervision of testing and putting the plant into smooth operation is done by chemical engineers. They also usually supervise normal operating and testing during production.

Most chemical engineers are in the above work. Others are found in related fields such as teaching, pure research, and technical sales.

UNIT OPERATIONS AND PROCESSES

The steps in the production of every chemical may be divided into three major groups. With few exceptions, the focal point of every plant is the *reactor*, where a *chemical* change from reactants to products is caused to occur.

Before the reactants enter the reactor, they may pass through numerous pieces of equipment. The primary function of this equipment is to place the reactants at the proper temperature, pressure, composition, purity, and phase to meet the design requirements of the reactor.

When the products leave the reactor they also must be processed. Often a mixture of products, contaminants, and unused reactants must be treated to obtain the various products in sufficiently pure form for the market.

In general, all the equipment except the reactor is used to cause *physical* changes—blending, separating, heating, cooling, pumping, etc.

The various physical operations, such as fluid flow, heat transmission, and distillation, are called *unit operations*. The reason for such classification is that the principles of any operation, such as distillation, are the same regardless of other differences which may exist between two plants. Chemical reactions may be classified as oxidation, nitration, hydrogenation, etc., and are divided into *unit processes*. You can accumulate the most comprehensive knowledge of the field if you learn the relatively few fundamental principles concerning these operations and processes. You can then learn rather easily the peculiarities of a particular application once you are working in the field.

FUNDAMENTALS

While the unit operations and processes are the building blocks of any chemical plant, these are in themselves often quite empirical. The calculations are based on generalized equations and correlations of laboratory and plant data. While these are essential to the rapid solution of practical problems, the engineer must recognize that all generalized relationships must rest on sound fundamental background. For this reason, fundamental courses, like stoichiometry, must be studied and understood before undertaking a study of "applied" courses.

From the fundamental standpoint, the solution of almost every chemical-engineering problem, whether a unit operation or process, includes several phases:

1. Quantities of reactants and products to be processed must be known. It is for this purpose that stoichiometry is studied.

2. Quantities of energy, particularly heat and certain types of work, must be evaluated. This material is thermodynamics. The broader

interpretation of stoichiometry, assumed in this book, includes heat balances as a matter of convenience.

3. Rates of reaction and material transfer must be known. In the broader sense, this may be called "kinetics." Usual courses in kinetics are actually chemical kinetics, where most interest is given to rates of chemical reactions. Rates of physical processes are studied as part of unit operations. Much work is presently being done on fundamental studies of mass, momentum, and energy transfer.

These three stages of a problem must be considered in practically every case. Sometimes the engineer is interested in predicting or evaluating the performance of an existing piece of equipment. At other times the equipment is to be built or purchased, and the final stage of the problem is equipment design. From the physical properties of the chemicals and materials of construction and from the basic principles underlying unit operations and unit processes, the engineer is able to specify equipment which will handle the proper amount of material, remove or add the necessary energy in the proper form and at the required rate, and allow sufficient time for reaction. (Since this specification usually leads to construction or purchase of equipment, design engineers often include economic balances as a fourth major category of fundamentals.)

The above steps cannot always be considered individually. Both the theoretical degree of completion and the rate of a reaction are dependent on operating conditions, while these conditions themselves are dependent on equipment size and shape and on the materials of construction. Complex problems can often be solved only with the most advanced mathematics.

CLASSIFICATION OF UNIT OPERATIONS

As mentioned above, unit operations are physical in nature. Their purpose is to process materials—reactants and products—to desired specifications of temperature, pressure, composition, and phase. From the standpoint of purpose, they fall into five major divisions:

1. Fluid flow
2. Heat transmission
3. Blending operations, such as agitation and mixing
4. Separation operations, such as distillation, extraction, absorption, adsorption, evaporation, crystallization, humidification, drying, filtration, and centrifugation
5. Solids handling, such as crushing, grinding, screening, and fluidization

There is no clear division between some of the operations. Continuous-evaporator calculations, for example, require fluid-flow equations

to determine pipe and pump sizing and heat-transfer equations to size the steam coils and condenser. In some cases crystallization may occur in the evaporator. It is thus to your advantage to look upon an evaporator as a piece of equipment where the processes of fluid flow, heat transmission, and possibly crystallization are utilized to effect a change in the composition of a solution. Any special equations which may be developed to simplify evaporation calculations can be shown to have an origin in the other operations mentioned.

It is not the purpose of this text to explore the field of unit operations. Thus the rest of this chapter is devoted to illustrations of the use of material and heat balances in a few representative cases. An extensive study of unit operations shows that there are many short cuts which can be taken to simplify the calculations. The use of such approaches is not advisable until the bases of them are clearly understood. Consequently, the sample problems are often solved by rather laborious means, chosen specifically to illustrate application of principles.

FLUID FLOW

This topic is considered first in most chemical-engineering unit-operations courses. The engineer must be familiar with the principles of fluid flow because it is necessary in every plant to transport reactants and products to various parts of the plant for processing. In most cases these materials are fluid, i.e., liquid or gaseous. The engineer must be able to determine sizes and types of piping and pumps to move the correct quantities of materials. The basic fundamentals of fluid flow are thermodynamic and kinetic in nature, and stoichiometry is little used here.

One principle of value, however, is a direct consequence of the law of conservation of matter; this is the *equation of continuity*. It is frequently used with thermodynamic and empirical relationships in the derivation of important equations. Basically, it is a mathematical statement of the obvious fact that the mass rate of flow is constant in a pipe where a fluid is flowing under steady-state conditions. Consider the following example.

Example 5-1. At one point in a 4-in. ID pipeline a gas at 20 psia and 30°C has an average velocity of 8 ft/sec. At some distance downstream, on the outlet side of a compressor, the gas passes through a venturi meter (a flow-measuring device). The gas in the throat of the venturi, which has an ID of 1.5 in., is at 50 psia and 40°C. What is the velocity of the gas in the throat, assuming that the perfect-gas law is valid?

Solution. Since the operation described is purely physical, it seems evident that the moles of gas passing the upstream point during any

time interval is equal to the moles passing through the throat in the same time interval. This is the *equation of continuity* for this problem. Mathematically,

$$N_1 = N_2$$

where N = number of moles/unit time and subscripts 1 and 2 refer to upstream and downstream, respectively.

Letting u = velocity, ft/sec
V = molar volume, ft³/lbmole
S = cross-sectional area, ft²

the term uS/V has the units of mole/sec and thus represents the rate of flow of the gas. From the equation of continuity,

$$\frac{u_1 S_1}{V_1} = \frac{u_2 S_2}{V_2}$$

and thus

$$u_2 = (u_1)\left(\frac{S_1}{S_2}\right)\left(\frac{V_2}{V_1}\right)$$

The value $(D_1/D_2)^2$ may be substituted for S_1/S_2, where D represents the diameter. (Note that any units may be used for D, as long as the same units are used for D_1 and D_2.)

The values of V_1 and V_2 may be calculated from the perfect-gas law as

$$V = \frac{RT}{p}$$

and thus

$$\frac{V_2}{V_1} = \left(\frac{T_2}{T_1}\right)\left(\frac{p_1}{p_2}\right)$$

Substituting in the equation,

$$u_2 = \left(\frac{8 \text{ ft}}{\text{sec}}\right)\left(\frac{4}{1.5}\right)^2\left(\frac{313}{303}\right)\left(\frac{20}{50}\right) = \frac{23.5 \text{ ft}}{\text{sec}}$$

HEAT TRANSMISSION

This is usually considered after fluid flow in chemical-engineering courses. As in the previous case, the fundamentals are mainly thermodynamic and kinetic in nature.

The engineer is interested in heat transfer because most chemical processes are not carried out at room temperature. Reactants and products must be heated or cooled. Some reactions are exothermic, and heat must be removed; others are endothermic, and heat must be supplied. The engineer must calculate the heat quantities and rates. He must then employ the numerous theoretical and empirical relationships of this field to design and operate equipment to meet the requirements of his process.

Heat balances were discussed in Chap. 4, and typical examples of heat exchange were illustrated in the problems.

SEPARATION OPERATIONS

By far the largest group of operations may be classified as separation. These include physical processes where two or more phases separate, such as filtration, dust collection, and decantation. There are processes where a material may move from one phase to another because of a greater affinity for the second phase. Illustrative of this class are extraction, absorption, and drying. Some processes, such as distillation and crystallization, depend on a tendency for one material in a mixture to separate into another phase under the influence of heat or of change in concentration. There are many similarities between many of these operations, and it is unnecessary to classify them into one or another group except for purposes of illustration.

From the standpoint of material and energy balances, there are no new principles in unit operations which have not already been presented. There are, however, numerous aids to calculation which permit more rapid solution of problems. Some of the more important of these will be presented in subsequent pages. There are also certain types of processing involving physical layout of equipment which are of practical significance. These will be introduced at appropriate points in the chapter.

Evaporation. We have chosen to discuss in some detail the common separation operation of evaporation because it clearly illustrates important stoichiometric principles. In general, this operation may be defined as the separation of a volatile solvent from a nonvolatile solute by vaporization of the solvent. In most practical cases the solvent is water; consequently the solute is the valuable product, and usually no attempt is made to recover the solvent.

Evaporators come in many sizes, shapes, and types. It is not within the scope of stoichiometry to describe these many types. From the standpoint of making material and energy balances, the type of evaporator is relatively unimportant. Most evaporators are merely physical variations of the simplest type assumed in our calculations.

Since the purpose of an evaporator is to vaporize some or all of the solvent from a solute, it is evident that the basic evaporator must consist of a means of supplying weak solution (feed), a means of removing strong solution (concentrate) and/or crystals, and a means of removing the vaporized solvent (evaporate). A source of heat, usually steam, must be available, and there must be some sort of heat-transfer surface so that this heat will pass from the steam to the boiling solution. The calculations which must usually be made on an evaporator include over-all

material and heat balances, so that relative quantities of feed, concentrate, and steam may be determined. Rate equations are also used to determine the size of equipment for a given amount of evaporation or amount of evaporation to be obtained from an existing piece of equipment. A sketch of an evaporator, satisfactory to aid in making material and heat balances, is given in Fig. 5-1.

The figure shows a continuous evaporator. Some evaporation processes are carried out batchwise, but continuous operation is used wherever possible. The equations derived below apply to the continuous case.

Except for very rare cases, all concentrations in evaporation are expressed on a weight basis. The following nomenclature will be used:

F = feed, lb/hr
E = evaporate, lb/hr
C = concentrate, lb/hr
S = steam, lb/hr
z = weight fraction of solute, lb solute/lb solution
H = enthalpy, Btu/lb
t = temperature, °F
c_p = specific heat, Btu/(lb)(F°)
Subscripts F, E, C, and S refer to these streams

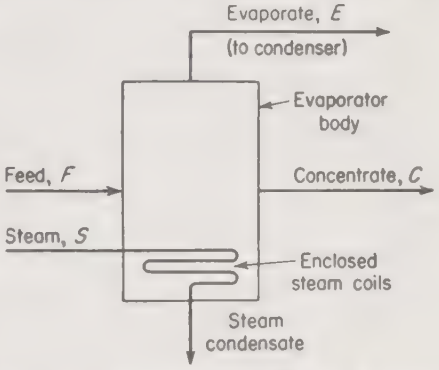


FIG. 5-1. Schematic diagram of evaporator.

Two material balances may be made:

Total: $F = E + C$
Solute: $Fz_F = Cz_c$

The heat balance may be written as an enthalpy balance for this system. Thus, heat in is the sum of enthalpies of the steam and feed:

$$\text{Heat in} = SH_{S(\text{in})} + FH_F$$

Heat out is the sum of enthalpies of condensed steam, evaporate, and concentrate, plus any losses from the system:

$$\text{Heat out} = SH_{S(\text{out})} + EH_E + CH_C + \text{losses}$$

At steady state the two may be equated:

$$SH_{S(\text{in})} + FH_F = SH_{S(\text{out})} + EH_E + CH_C + \text{losses}$$

In order to solve problems, we must express the enthalpies in terms of measurable quantities, such as temperature, pressure, and concentration. As mentioned in the previous chapter, when enthalpies are added as in

the above equation, they must all be referred to the same basis. Suppose that we choose as base conditions liquid water and solid solute at 25°C and 1 atm pressure. We may assign the water and solute enthalpy values of zero at these conditions. Now examine the nature of each quantity in turn, remembering that enthalpy is affected by temperature, pressure, and composition.

$H_{S(\text{in})}$ is the enthalpy of the entering steam minus the enthalpy of liquid water at 25°C and 1 atm. $H_{S(\text{out})}$ is the enthalpy of the leaving condensed steam minus the enthalpy of liquid water at 25°C and 1 atm. The amount of heat obtained from the steam is $(S)(H_{S(\text{in})} - H_{S(\text{out})})$. Note that this term could be obtained from tabulated values of enthalpies of water and steam based on any assumed base conditions, since the base enthalpy does not appear in the final expression.

H_F is the enthalpy of the feed. We may establish its value by standard thermochemical means:

$H_F = \Delta H$ of solution + ΔH for temperature change
+ ΔH for pressure change

ΔH of solution is the standard integral heat of solution at 25°C and 1 atm.

ΔH for temperature change is $\int_{t_b}^{t_F} c_p \, dt$, where t_b = base temperature (25°C).

ΔH for pressure change is ordinarily negligible for a liquid solution. Assigning an average heat capacity to the feed,

$$H_F = \Delta H_{\text{soln},F} + c_{p_F}(t_F - t_b)$$

Similarly,

$$H_C = \Delta H_{\text{soln},C} + c_{p_C}(t_c - t_b)$$

The value H_E, since it applies to pure water vapor, contains no term for heat of dilution. As in the case of the steam, it merely represents the difference in enthalpy between the evaporate at existing conditions and liquid water at the base conditions. We may, however, represent it as follows:

$$H_E = \Delta H \text{ due to pressure} + \int_{t_b}^{t_p} c_{p(\text{liq})} \, dt + \Delta H_{\text{vap},p} + \int_{t_p}^{t_E} c_{p(\text{vap})} \, dt$$

In this equation the ΔH due to pressure is the enthalpy change for changing the pressure on liquid water at 25°C from 1 atm to the pressure in the evaporator and is negligible. The water is heated to t_p, the boiling point *at the pressure in the evaporator*. The enthalpy change for this step is $\int_{t_b}^{t_p} c_{p(\text{liq})} \, dt$. Since the heat capacity of liquid water is essentially 1, we may write this term as $(1)(t_p - t_b)$. The value $\Delta H_{\text{vap},p}$ is the latent

heat of vaporization *at the pressure p*. The final term represents sensible heat (in this case, superheat) in the vapor. Here also an average heat capacity may be used.

All these terms combine into the following equation:

$$S(H_{S(\text{in})} - H_{S(\text{out})}) + F[\Delta H_{\text{soln},F} + c_{p_F}(t_F - t_b)] = C[\Delta H_{\text{soln},C} + c_{p_c}(t_c - t_b)] + E[(1)(t_p - t_b) + \Delta H_{\text{vap},p} + c_{p(\text{vap})}(t_E - t_p)] + \text{losses}$$

Rearranging the equation, and substituting $t_c = t_E$, the following is obtained:

$$S\,\Delta H_S + F\,\Delta H_{\text{soln},F} - C\,\Delta H_{\text{soln},C} + Fc_{p_F}(t_F - t_c) = (Cc_{p_c} + E - Fc_{p_F})(t_c - t_b) + E[(t_p - t_c) + \Delta H_{\text{vap},p} + c_{p(\text{vap})}(t_c - t_p)] + \text{losses}$$

This is an accurate heat-balance equation for evaporation calculations. You should note that it was obtained by exactly the same type of analysis as was used in practically all the thermochemical problems of the previous chapter. The equation is somewhat difficult to use, however, and we shall proceed to find a simpler form. This form will be the one used in industry in most cases. It involves certain assumptions which must be clearly understood.

The first assumption involves the choice of base temperature. You will note that t_b appears in the equation explicitly in only one term. It appears implicitly in the two heat-of-solution terms. We originally chose 25°C as t_b since most thermochemical data are available at this temperature. The equation is not changed in form if we define $t_b = t_c$, but one term is removed. Rewriting and rearranging,

$$S\,\Delta H_S + Fc_{p_F}(t_F - t_c) = E\,\Delta H_{\text{vap},p} + C\,\Delta H_{\text{soln},C} - F\,\Delta H_{\text{soln},F} - E(t_c - t_p)(1 - c_{p(\text{vap})}) + \text{losses}$$

Now, implicitly, the heats of solution must be evaluated at t_c. It is usually assumed that the grouping

$$C\,\Delta H_{\text{soln},C} - F\,\Delta H_{\text{soln},F} - E(t_c - t_p)(1 - c_{p(\text{vap})}) + \text{losses}$$

is negligible compared with other terms in the equation. It is usually small and positive. The equation remaining is

$$S\,\Delta H_{\text{vap},S} + Fc_{p_F}(t_F - t_c) = E\,\Delta H_{\text{vap},p}$$

Note that we have written $\Delta H_{\text{vap},S}$ for ΔH_S. This means that we usually assume that only the heat of vaporization of the steam is obtained when the steam is condensed. Superheat and subcooling are ignored. Since

neglecting the small positive grouping on the right makes this side smaller, the use of a smaller ΔH for the steam is justified.

If we rewrite the equation

$$S\,\Delta H_{vap,S} = Fc_{pF}(t_c - t_F) + E\,\Delta H_{vap,p}$$

it corresponds to a word equation "The heat furnished by the steam is equal to the heat needed to heat the feed to the boiling point plus that needed to vaporize the desired amount of water from the solution."

In the development of the equations three temperatures, t_p, t_E, and t_c, appeared which need further explanation. t_c is the actual temperature in the boiling solution. t_E is the temperature of the vapors leaving the solution and is equal to t_c. t_p is the boiling point of water at the pressure in the evaporator. The difference $t_c - t_p$ is called the *boiling-point rise.* The BPR, as it is usually written, is due to vapor-pressure lowering of the solvent by dissolved solutes. Methods of calculating it are not a part of stoichiometry. We have assigned values to the BPR where it is necessary to work the problems in this text. You should note that, in the derivation of the simplified equation, we separated the term $E\,\Delta H_{vap,p}$ from two other terms containing E. These two terms, combined with $E\,\Delta H_{vap,p}$, give the heat of vaporization at t_c, that is,

$$E[(t_p - t_c) + \Delta H_{vap,p} + c_{p(vap)}(t_c - t_p)] = E\,\Delta H_{vap,t_c}$$

It is customary to neglect the two sensible-heat terms. Usually the higher the BPR, the greater the heat-of-solution effect. The heat of vaporization at the *pressure* is higher than that at the *temperature* in the evaporator. The use of this higher value compensates to a great extent for neglecting the heat-of-solution terms.

To review, then, the final equation presented is valid in most cases. It is customary to assume that the steam gives up only its heat of vaporization; superheat and subcooling are neglected. The heat of vaporization of the evaporate is determined at the *pressure* in the evaporator. The examples following will illustrate the general method of solution and the validity of the assumptions made.

Example 5-2. A sodium hydroxide solution is being evaporated from 35.7%w NaOH to 52.6%w. Using the following information, calculate the steam required to concentrate 100 lb of entering solution. The feed enters at 150°F. The evaporate is removed to a condenser which maintains a temperature of 140°F. The vapor condensing at this temperature maintains the evaporator body at its vapor pressure, 2.89 psia. Because of the high concentration of NaOH in the boiling solution (assumed to be 52.6%, the same as the product), the BPR is 83 F°. The inlet and outlet solutions have the following properties:

	%w	$\frac{\text{mole } H_2O}{\text{mole NaOH}}$	ΔH_{soln} at 25°C, cal/gmole NaOH	Average c_p, cal/(g)(C°)
Inlet	35.7	4	−8400	0.80
Outlet	52.6	2	−4600	0.78

Heat is supplied by steam entering at 30 psia and 270°F. The steam is superheated. It condenses at 30 psia and its saturation temperature of 250.3°F. The condensed steam is cooled to 235°F before it leaves the evaporator. The following data are from the steam tables:

Conditions	Enthalpy, relative to liquid water at 32°F, Btu/lb	ΔH_{vap}, Btu/lb
77°F, liquid	45	
140°F	.....	1014.1
223°F	.....	963.2
223°F, 2.89 psia, vapor	1160	
235°F, saturated liquid	203.3	
30 psia	.....	945.3
30 psia, saturated liquid	218.8	
30 psia, saturated vapor	1164.1	
270°F, 30 psia	1174.2	

Enthalpy data are available for NaOH-H_2O solutions above liquid water and solid NaOH at 32°F:

Conditions	*H, Btu/lb solution*
35.4%w, 150°F	−46.6
52.6%w, 223°F	+33.6

(Note that pressure effects on the enthalpy of the solution are negligible.)

Solve the problem using (*a*) the simplified equations, (*b*) thermochemical equations, and (*c*) enthalpy data for the system.

Solution a. Using usual simplifying assumptions:

Basis: 100 lb entering solution

Material balance:

$$Fz_F = Cz_c$$

$$C = \frac{(100)(0.357)}{0.526} = 67.8 \text{ lb concentrate}$$

$$F = E + C$$

$$E = 100 - 67.8 = 32.2 \text{ lb evaporate}$$

Heat balance:

$$S\,\Delta H_{vap,S} = Fc_{pF}(t_C - t_F) + E\,\Delta H_{vap,p}$$

$$S = \frac{(100)(0.80)(223 - 150) + (32.2)(1014.1)}{945.3}$$

$$S = \frac{41{,}700 \text{ Btu}}{945.3 \text{ Btu/lb}} = 44.1 \text{ lb steam}$$

Solution b. By thermochemical calculations. The heat load may be calculated by a series of steps for which enthalpy values may be obtained. (Note that pressure changes are neglected.)

1. Cool entering solution to 25°C (77°F).

$$\Delta H = (100 \text{ lb})\left(\frac{0.80 \text{ Btu}}{(\text{lb})(\text{F°})}\right)(77 - 150)\text{F°} = -5840 \text{ Btu}$$

2. Separate water from solution at 77°F.

$$\Delta H = [-4600 - (-8400)]\left(\frac{\text{cal}}{\text{gmole}}\right)\left(\frac{1.8 \text{ Btu/lbmole}}{\text{cal/gmole}}\right)\left(\frac{35.7 \text{ lbmole}}{40}\right) = 6110 \text{ Btu}$$

3. Heat the concentrate to 223°F.

$$\Delta H = (67.8 \text{ lb})\left(\frac{0.78 \text{ Btu}}{(\text{lb})(\text{F°})}\right)(223 - 77)\text{F°} = 7720 \text{ Btu}$$

4. Vaporize and heat water from 77° to 223°F, 2.89 psia.

$$\Delta H = \left(\frac{(1160 - 45) \text{ Btu}}{\text{lb}}\right)(32.2 \text{ lb}) = 35{,}900 \text{ Btu}$$

Adding these four quantities, the total heat needed is 43,890 Btu. The estimate in part *a* is only about 5% low. If we use the larger enthalpy change for the steam (including superheat and subcooling),

$$S = \frac{43{,}890}{1174.2 - 203.3} = 45.2 \text{ lb steam}$$

and the previously calculated value of 44.1 is low by only 2.4%.

Solution c. By use of enthalpy diagrams. The over-all reaction is

$$\left\{\begin{matrix}100 \text{ lb } 35.7\%\text{w NaOH,} \\ 150°\text{F, 1 atm}\end{matrix}\right\} \rightarrow \left\{\begin{matrix}67.8 \text{ lb } 52.6\% \text{ NaOH,} \\ 223°\text{F, 2.89 psia}\end{matrix}\right\} + \left\{\begin{matrix}32.2 \text{ lb water vapor,} \\ 223°\text{F, 2.89 psia}\end{matrix}\right\}$$

For steady flow, $Q = \Delta H$. If we have enthalpy values for inlet and outlet streams available, we may merely add these algebraically and obtain

the answer. Tables or plots of such values are available for some systems. Values appropriate to this problem are given in the statement. All values must be on the same basis.

$$\Delta H = (32.2)(1160) + (67.8)(33.6) - (100)(-46.6) = 44{,}340 \text{ Btu}$$

This value agrees closely with the one from part *b*.

At this point it seems advisable that we review our situation to place our work in its proper perspective. In the discussion of evaporation we have devoted more space to the development of the equations than we shall do for the other unit operations. We have done this for the purpose of showing how a process may be analyzed from basic material- and energy-balance considerations. We have then simplified the equations to the ones usually encountered in practice. In doing so, we have made certain assumptions which restrict the range of usefulness of the equations. Finally, we have given a numerical example to show that these assumptions are reasonable.

You will find, in all unit operations, that simplified equations are usually preferred. These equations give answers which are close enough to the true answers that they may be safely used in practical engineering work. The engineer saves time when he uses the simplified equations in preference to the more complex rigorous equations. Since time saved is money saved in industry, short cuts are always used when it is safe to do so. The important point to recognize here is that there are almost always rigorous ways and simplified ways to perform calculations. The choice of which to use is a matter of economics and is made by the engineer, based on his judgment and experience. When in doubt, use the rigorous method until your practical experience is such that you may safely choose easier ways.

There are other important implications in our work to date. We have mentioned more than once that we cannot calculate size of equipment solely from the material and energy balances. We may be even further restricted by chemical and physical properties of the materials with which we are working.

Suppose, for example, that we work out a problem like Example 5-2. This tells us the steam requirement for 100 lb of entering solution. Suppose now that we know that 10 tons of entering solution must be processed per hour. We could then calculate the total steam required per hour. Now, let the problem be to specify a particular evaporator to do this job. We cannot determine the size from the calculations we have made. This requires a knowledge of heat-transfer coefficients, which are studied in unit operations. A further consideration in the choice of evaporator is the material of construction. This choice can be made only when you know the corrosion characteristics of the various possible

materials. Finally, there are many physical arrangements of equipment which would do the job. A choice must be made here also; this requires a thorough knowledge of the relative advantages and disadvantages of the different types. These might be based on ease of installation and replacement, ease of cleaning the unit, possibility of using the unit for other purposes, costs of purchase and operation, delivery times, etc. It is evident that much more than just the material and energy requirements is needed before the unit can actually be specified.

To continue our example, let us suppose that we have a unit which will perform the necessary separation on 10 tons of feed per hour. We might now ask, "How much steam is required for 20 tons of feed per hour?" The answer is easy; twice as much steam is required for 20 tons as for 10. However, an evaporator capable of concentrating the 10 tons may not be satisfactory for 20 tons. In fact, it may not do the job at all. It is possible that we could change the operating conditions, such as the amount of vacuum and the steam pressure, to process the 20 tons, but we cannot process the 20 tons in the 10-ton unit under exactly the same conditions as for 10 tons/hr. Thus we have a situation where there is no complication as far as material and energy balances are concerned, but a practical answer as to how to operate the unit (or whether it will work or not) demands knowledge of evaporation not gained from simple stoichiometric studies.

Let us consider another complication which might arise in such calculations. Suppose that we have made the calculations for sodium hydroxide solutions, as in the example. Then we find that an error has been made and that the calculations were to have been made for a different solute, such as sodium chloride or potassium nitrate. Can we say that the same amount of steam is necessary for these other solutes? The chances are high that we cannot. The other solutes have different heats of solution; the specific heats of their solutions are different. Furthermore, these materials may not be as soluble as sodium hydroxide, and we might find that crystallization would occur if we tried to make the outlet solution as concentrated as the outlet sodium hydroxide solution. We might find that some solutes would crystallize out as solid solute and that others would crystallize out with water of hydration. Thus our material and heat balances may be different from those for sodium hydroxide and can be made only if we have knowledge of the chemical and physical behavior of these solutes in solution.

Assuming that we could make the material and energy balances and that these were similar to those for the sodium hydroxide, we could still not say that the evaporator suitable for sodium hydroxide solutions would be suitable for the other solutions. Perhaps the heat-transfer coefficients would be considerably different, because of different properties of the

solutions. Perhaps these other solutes would have different corrosive tendencies, requiring entirely different materials of construction. They might have different tendencies to scale or to deposit out on heating tubes, requiring a different physical arrangement of the equipment for practical purposes of cleaning and repairing the equipment. All these considerations require studies of properties of chemicals, materials of construction, and unit operations, and questions based on these considerations cannot logically be answered just on a study of stoichiometry.

Inventory Change. There is frequently a fundamental difference between the calculations made in order to design or specify a piece of equipment and the calculations made to evaluate the performance of an existing piece of equipment. This difference is due to the fact that most plant equipment is designed on the assumption that it will operate continuously at steady state, whereas actual performance, while continuous, may not be steady-state. We may investigate these implications by considering first the simple word equations of material and energy balances.

The equation forming the basis of all our calculations is

$$\text{Input} - \text{output} = \text{accumulation}$$

We have pointed out previously that, for a batch process, where material is being added and none removed (as in blending a batch of paint),

$$\text{Input} = \text{accumulation}$$

For a batch process where material is being removed only (as in draining a solution from a batch of crystals),

$$-\text{Output} = \text{accumulation} = -\text{depletion}$$

For the steady-state continuous case, such as a continuous evaporator,

$$\text{Input} = \text{output}$$

This equation may be applied to the total amount of material for any unspecified amount of time, or it may be put on a rate basis:

$$\text{Rate of input} = \text{rate of output}$$

It is this form which is frequently most valuable and which would be used by a design engineer in selecting the proper piece of equipment for a given job. However, in evaluating the performance of existing equipment, even when it is operating continuously, we frequently find inventory changes have taken place. Thus, there has been an accumulation (or depletion) of material within the system, and we are forced to use the equation

$$\text{Input} - \text{output} = \text{accumulation}$$

Before going to some examples, we might investigate the mathematical

significance of some of the statements which have been made. Basically, the rate at which material enters or leaves a unit can be given as a derivative; the total amount of material which has entered or which has left can be expressed as an integral. Let us define I, O, A, and D as input, output, accumulation, and depletion, respectively, for ease of writing the equations. Then, the basic equation is

$$I - O = A$$

Differentiating to get rates,

$$\frac{dI}{d\theta} - \frac{dO}{d\theta} = \frac{dA}{d\theta}$$

where θ = time.

For a total period of time θ_t,

$$I = \int_0^{\theta_t} \frac{dI}{d\theta}\, d\theta$$

and, if the rate $dI/d\theta$ is constant,

$$I = \frac{dI}{d\theta}(\theta_t - 0) = \frac{dI}{d\theta}\,\theta_t$$

This is an obvious equation, at least in word form. Thus, if 5 tons/hr of solution enters an evaporator, and it runs 24 hr/day, we calculate

$$I = (5)(24) = 120 \text{ tons}$$

during the one-day period.

If the rate is not constant, we may still calculate I if we know the rate as a function of time. It is for this reason that industrial plants have so many instruments which record rates vs. time. We may write the same sort of equations for O, A, and D in either batch or continuous processes.

For the general case, we may write our input-output equation as

$$\int_o^{\theta_t} \frac{dI}{d\theta}\, d\theta - \int_o^{\theta_t} \frac{dO}{d\theta}\, d\theta = \int_o^{\theta_t} \frac{dA}{d\theta}\, d\theta$$

This may appear as unnecessary symbolism, but it does add some mathematical validity to the treatment we wish to develop. Let us consider two problems in evaporation to illustrate our point.

Example 5-3. An evaporator operating continuously is tested over a 5-hr period. Both the evaporate and concentrate streams include integrating, or totalizing, meters from which the total amount of material which has passed through the meters may be read. The rate of output is controlled so that a constant composition (equal at all times to the composition in the evaporator proper) is maintained. The following readings are taken:

Time, hr	Input meter, total lb	Output meter, total lb
0	145,600	327,400
5	167,300	337,910

The input contains 5%w solids. The concentration within the evaporator and in the outlet stream is 10%w. The diameter of the vertical cylindrical evaporator body is 4 ft. The specific gravity of the solutions may be considered 1 for simplicity.

a. How much water is evaporated during the test?

b. How much does the level of material within the evaporator change during the test?

Solution

a. If the evaporator nomenclature previously defined is used,

$$\text{input} = \text{feed} = F$$

and output = concentrate = C. In this case we let F and C refer to total pounds of material during the test. (We must also consider evaporate E as an output in calculating accumulation.)

$$F = 167{,}300 - 145{,}600 = 21{,}700 \text{ lb}$$
$$C = 337{,}910 - 327{,}400 = 10{,}510 \text{ lb}$$

Since we know the concentrations, we may calculate E. In this case, since there is some accumulation and its concentration is the same as the concentrate,

$$0.05F = 0.10(C + A)$$

and

$$F = (C + A) + E$$

From the first equation,

$$C + A = 0.5F$$

Therefore, from the second equation,

$$E = 0.5F = 10{,}850 \text{ lb evap}$$

b.

$$C + A = 10{,}850 \text{ lb}$$

Since C is known to be 10,510 lb,

$$A = 340 \text{ lb}$$

and

$$\frac{340 \text{ lb}}{62.4 \text{ lb/ft}^3} = 5.45 \text{ ft}^3 \text{ accumulation}$$

The cross-sectional area of the evaporator body is $\pi D^2/4 = 12.6$ ft^2.

Therefore, the rise in level is

$$\frac{5.45 \text{ ft}^3}{12.6 \text{ ft}^2} = 0.432 \text{ ft} \approx 5.2 \text{ in.}$$

Example 5-4. The same test is run as in Example 5-3. In this case, however, the input and output lines are not equipped with totalizing meters. Instead, rotameters are used. These indicate instantaneous rates of flow. By an electronic circuit the readings are transmitted to recording instruments which plot a continuous record of rate vs. time. Scale factors within the instruments are such that the readings, in volumetric units, are recorded in weight units. Selected readings are as follows:

Time, hr	Feed rate, lb/hr	Concentrate rate, lb/hr
0	5000	2500
1	4850	2400
2	4600	2250
3	4250	2050
4	3800	1800
5	3250	1500

As before, the diameter is 4 ft, and the specific gravity is 1. The inlet concentration is 5%w, and the concentration of the material in the evaporator and in the concentrate stream is 10%w. Calculate the following:

a. The total feed
b. The total concentrate
c. The amount evaporated
d. The accumulation
e. The rise in level in the evaporator body
f. The rate of evaporation as a function of time
g. The level in the evaporator as a function of time

Solution

a.

$$F = \int_0^5 \frac{dF}{d\theta}\, d\theta$$

We do not know the feed rate as a mathematical function of time and therefore cannot integrate the expression analytically. A graphical or numerical integration is satisfactory. Using the trapezoid rule,

$$F = (1)\left(\frac{5000}{2} + 4850 + 4600 + 4250 + 3800 + \frac{3250}{2}\right)$$

$$F = 21{,}625 \text{ lb}$$

b. $$C = (1)\left(\frac{2500}{2} + 2400 + 2250 + 2050 + 1800 + \frac{1500}{2}\right)$$
$$C = 10{,}500 \text{ lb}$$

c. As before, $E = 0.5F$.

d.
$$E = 10{,}813 \text{ lb}$$
$$C + A = 0.5F = 10{,}813 \text{ lb}$$
$$A = 313 \text{ lb}$$

e.
$$\frac{313 \text{ lb}}{62.4 \text{ lb/ft}^3} \div 12.6 \text{ ft}^2 = 0.398 \text{ ft} \approx 4.8 \text{ in.}$$

Level rises 4.8 in.

f. Since it was stated that the concentrate and accumulation at all times have a concentration of 10%w, the rate of evaporation must at all times be one-half the rate of feed. Thus we may tabulate the values:

Time, hr	0	1	2	3	4	5
Rate of evaporation, lb/hr	2500	2425	2300	2125	1900	1625

g. The level in the evaporator as a function of time may be calculated in exactly the same manner as was the final level in parts *d* and *e*. Again using the trapezoid rule, a sample calculation for the first hour is shown.

$$F = \frac{5000 + 4850}{2} = 4925 \text{ lb}$$
$$C = \frac{2500 + 2400}{2} = 2450 \text{ lb}$$
$$E = (0.5)(4925) = 2462.5 \text{ lb}$$
$$A = 4925 - (2450 + 2462.5) = 12.5 \text{ lb}$$
$$\text{Rise in inches} = \frac{(12.5)(12)}{(62.4)(12.6)} = 0.19 \text{ in.}$$

In a similar manner the rest of the data are calculated. The results are summarized in the table.

Time period, hr	*F*, lb	*C*, lb	*E*, lb	*A*, lb	Rise, in.	Total rise, in.
0–1	4,925	2,450	2,462.5	12.5	0.19	0.19
1–2	4,725	2,325	2,362.5	37.5	0.57	0.76
2–3	4,425	2,150	2,212.5	62.5	0.95	1.71
3–4	4,025	1,925	2,012.5	87.5	1.33	3.04
4–5	3,525	1,650	1,762.5	112.5	1.72	4.76
	21,625	10,500	10,812.5	312.5	4.76	

The examples illustrate some points regarding total (or integral) meters and rate (or differential) meters. The same over-all information may

be obtained from either. In this case, we were interested in the total water evaporated during the test period. The total-flow readings are easier to work with than the differential readings, which have to be integrated in some manner. However, if we are interested in the rates in a process, then the differential readings are much easier to use and are more reliable. For example, in Example 5-3, the only rate figure we could determine would be the average over the entire time period. In this case it would have been 21,700 lb/5 hr = 4340 lb/hr for the feed and one-half this value for the evaporate. In the practical testing of equipment, the rate as a function of time might be important. (In an evaporator, for example, the rate usually drops off with time, because of scaling on the heating surfaces. A careful study of this rate will determine the most economical cycle of running and cleaning the evaporator to obtain maximum evaporation per day.) Such information cannot be obtained from total-flow readings taken at the beginning and end of a test period.

We can use integrating meters to obtain rates as a function of time if we take enough readings. Just as total flow is obtained by integrating differential-meter readings, we get flow rates by differentiating total-flow readings. In Example 5-4, had we used a total-flow meter instead of a rotameter, we might have obtained these data:

Time, hr.....	0	1	2	3	4	5
Feed, lb.....	0	4925	9650	14,075	18,100	21,625

To obtain true differential rates, we should fit these data to an equation, then differentiate the expression, and finally substitute various values of time to get the rates. Usually the curve-fitting takes more time than is warranted, and rates are obtained by taking differences. Thus, we set up a table to find these differences:

θ, hr	$\Delta\theta$, hr	F, lb	ΔF, lb	$\frac{\Delta F}{\Delta\theta}$, lb/hr
0		0		
	1		4925	4925
1		4,925		
	1		4725	4725
2		9,650		
	1		4425	4425
3		14,075		
	1		4025	4025
4		18,100		
	1		3525	3525
5		21,625		

These figures give average rates during short time intervals. Thus, 4425 lb/hr is the average rate during the time from 2 to 3 hr during the test. In plotting the data, we should be very close to correct if we should plot 4425 lb/hr as the rate at 2.5 hr, the average of 2 and 3.

A more complex case, from the standpoint of the arithmetic work involved, arises when the inventory changes for both total material and components. Principles involved are, of course, no different. Consider this example.

Example 5-5. In testing the performance of an evaporator, measurements are taken of the total amount of feed, total amount of material in the evaporator, and concentration of the material in the evaporator. The inlet concentration is constant at $Z_F = 0.05$ (5%w of salt). The outlet (concentrate) concentration is, at any instant, the same as that of the material in the evaporator.

From the data, calculate the total amount of concentrated solution, the total amount of water evaporated, and the average concentration of the concentrated solution as functions of time. Determine also the approximate rates of removal of water and concentrate as functions of time.

Data:

Time, θ, hr	Total feed, F, lb	Accumulation, A, lb	Concentration in evaporator, Z_A, lb salt/lb solution
0	0	5000	0.10
1	4,930	5000	0.0997
2	9,640	4980	0.0990
3	14,010	4910	0.0974
4	17,920	4760	0.0946
5	21,250	4500	0.0902

Solution

Define F = total feed, lb
A = accumulation, lb
E = evaporate (pure water), lb
C = concentrate, lb
Z_F = feed concentration, lb salt/lb solution
Z_A = concentration of accumulation (and instantaneous value of concentrate), lb salt/lb solution
θ = time, hr

At any time, the rate of accumulation is equal to the feed rate minus rate of output. This holds for both total mass of material and for the salt.

Thus

$$\frac{dF}{d\theta} - \left(\frac{dC}{d\theta} + \frac{dE}{d\theta}\right) = \frac{dA}{d\theta}$$

and

$$Z_F \frac{dF}{d\theta} - Z_A \frac{dC}{d\theta} = \frac{d(AZ_A)}{d\theta}$$

The two unknown quantities are C and E. We therefore wish to solve these equations for these quantities. Thus

$$\frac{dC}{d\theta} + \frac{dE}{d\theta} = \frac{dF}{d\theta} - \frac{dA}{d\theta}$$

and

$$\frac{dC}{d\theta} = \frac{Z_F}{Z_A}\frac{dF}{d\theta} - \frac{1}{Z_A}\frac{d(AZ_A)}{d\theta}$$

We may integrate the first equation to obtain

$$(C - C_0) + (E - E_0) = (F - F_0) - (A - A_0)$$

where C_0, E_0, F_0, and A_0 are values at time zero. All can be assumed zero except A_0, which is given as 5000 lb. The second equation integrates to

$$C - C_0 = Z_F \int_0^\theta \frac{1}{Z_A}\frac{dF}{d\theta}\,d\theta - \int_0^\theta \frac{1}{Z_A}\frac{d(AZ_A)}{d\theta}\,d\theta$$

These integrations cannot be performed analytically; consequently a numerical method must be used.

We will choose time intervals of 1 hr. Then

$$\int_0^1 \frac{dC}{d\theta}\,d\theta = \Delta C = C_1 - C_0$$

with similar expressions for ΔE, ΔF, and ΔA.

For the more complex integrals, we must choose some average values to perform the numerical operations. Thus,

$$Z_F \int_0^1 \frac{1}{Z_A}\frac{dF}{d\theta}\,d\theta = \frac{Z_F}{\bar{Z}_A}\Delta F$$

and

$$\int_0^1 \frac{1}{Z_A}\frac{d(AZ_A)}{d\theta}\,d\theta = \frac{1}{\bar{Z}_A}\Delta(AZ_A)$$

where $\bar{Z}_A$ is the average value of Z_A during the interval, defined as $(\frac{1}{2})(Z_{A_0} + Z_{A_1})$. We must again stress that these numerical-integration methods are approximations and that we have chosen to illustrate only the simplest one.

We may now write the working equations:

$$\Delta C = \frac{Z_F}{\bar{Z}_A}\Delta F - \frac{1}{\bar{Z}_A}\Delta(AZ_A)$$

and $\Delta E = \Delta F - \Delta A - \Delta C$.

Actual solution is best accomplished in tabular form. First we obtain ΔF, ΔA, $\bar{Z}_A$, and $\Delta(AZ_A)$. For example, for the period from 2 to 3 hr,

$$\Delta F = 14{,}010 - 9640 = 4370 \text{ lb}$$
$$\Delta A = 4910 - 4980 = -70 \text{ lb}$$
$$\bar{Z}_A = \tfrac{1}{2}(0.0990 + 0.0974) = 0.0982 \text{ (lb salt/lb solution)}$$
$$\Delta(AZ_A) = (4910)(0.0974) - (4980)(0.0990) = -14.8 \text{ lb salt}$$

Results for the entire test period are shown in the table.

θ	F	ΔF	A	ΔA	Z_A	$\bar{Z}_A$	AZ_A	$\Delta(AZ_A)$
0	0		5000		0.10		500	
		4930		0		0.0999		−1.5
1	4,930		5000		0.0997		498.5	
		4710		−20		0.0994		−5.5
2	9,640		4980		0.0990		493	
		4370		−70		0.0982		−14.8
3	14,010		4910		0.0974		478.2	
		3910		−150		0.0960		−27.9
4	17,920		4760		0.0946		450.3	
		3330		−260		0.0924		−44.4
5	21,250		4500		0.0902		405.9	

Next we calculate ΔC by

$$\Delta C = \frac{Z_F}{\bar{Z}_A}\Delta F - \frac{1}{\bar{Z}_A}\Delta(AZ_A)$$

For the time interval, 2 to 3 hr,

$$\Delta C = \left(\frac{0.05}{0.0982}\right)(4370) - \frac{(-14.7)}{0.0982} = 2376 \text{ lb}$$

and

$$C_3 = C_2 + \Delta C_{2-3} = 4905 + 2376 = 7281 \text{ lb}$$

Results are given in the next table.

Time interval, hr	ΔF	$\bar{Z}_A$	$\frac{Z_F}{\bar{Z}_A}$	$\frac{Z_F}{\bar{Z}_A}\Delta F$	$\Delta(AZ_A)$	$\frac{\Delta(AZ_A)}{\bar{Z}_A}$	ΔC	C
0–1	4930	0.0999	0.500	2465	−1.5	−15	2480	2,480
1–2	4710	0.0994	0.503	2370	−5.5	−55	2425	4,905
2–3	4370	0.0982	0.509	2225	−14.8	−151	2376	7,281
3–4	3910	0.0960	0.521	2035	−27.9	−291	2326	9.607
4–5	3330	0.0924	0.541	1800	−44.4	−480	2280	11,887

We may now calculate ΔE by

$$\Delta E = \Delta F - \Delta A - \Delta C$$

Again, for the period 2 to 3 hr,

$$\Delta E = 4370 - (-70) - 2376 = 2064 \text{ lb}$$

and $$E_3 = E_2 + \Delta E_{2-3} = 4755 + 2064 = 6819 \text{ lb}$$

Results are given in the next table

Time interval, hr	ΔF	ΔA	ΔC	ΔE	E
0–1	4930	0	2480	2450	2450
1–2	4710	−20	2425	2305	4755
2–3	4370	−70	2376	2064	6819
3–4	3910	−150	2326	1734	8553
4–5	3330	−260	2280	1310	9863

We have been asked also for the average concentration of the concentrate removed. We may express this mathematically by an equation exactly like the one used to find mean heat capacity:

$$\bar{Z}_C = \frac{\int_0^C Z_C \, dC}{\int_0^C dC} = \frac{\int_0^\theta Z_C \frac{dC}{d\theta} \, d\theta}{\int_0^\theta \frac{dC}{d\theta} \, d\theta}$$

The *instantaneous* value of Z_C is equal to Z_A.

To find $\bar{Z}_C$, we would have to use a numerical-integration method similar to that used for finding C. In doing this, we should be engaging in a mathematical pastime while ignoring a much simpler and more direct approach. The value $\bar{Z}_C$ is the average composition of the concentrate; thus it is the total salt in the concentrate divided by the total amount of concentrate. (This is exactly what the equation above says.) We have already determined the total amount of concentrate. We can find, by simple input and output calculations, the total salt in the concentrate. Thus, after 5 hr,

$$C = 11{,}887 \text{ lb}$$
$$F = 21{,}250 \text{ lb}$$
$$FZ_F = (21{,}250)(0.05) = 1062.5 \text{ lb salt}$$
$$AZ_A = 405.9 \text{ lb salt}$$

At zero time, $AZ_A = 500$ lb salt.

Then accumulation of salt during this time is

$$\Delta(AZ_A) = 405.9 - 500 = -94.1 \text{ lb}$$

Input − accumulation = output of salt

$$1062.5 - (-94.1) = 1156.6 \text{ lb}$$

and $$\bar{Z}_C = \frac{1156.6}{11887} = 0.0973$$

This calculation may also be put in tabular form. In this case, we are interested in the average composition of the entire output. Thus, we always measure changes from the beginning of the test period and not for 1-hr intervals.

Time, hr	F	FZ_F	AZ_A	$\Delta(AZ_A) = AZ_A - (AZ_A)_0$	C	$\bar{Z}_C = \frac{FZ_F - \Delta(AZ_A)}{C}$
1	4,930	246.5	498.5	−1.5	2,480	0.1000
2	9,640	482.0	493.0	−7.0	4,905	0.0996
3	14,010	700.5	478.2	−21.8	7,281	0.0993
4	17,920	896.0	450.3	−49.7	9,607	0.0984
5	21,250	1062.5	405.9	−94.1	11,887	0.0973

We are also asked for some approximate rates of evaporation and concentrate removal. These are estimated by

$$\frac{dE}{d\theta} \approx \frac{\Delta E}{\Delta \theta}$$

where $dE/d\theta$ represents the rate at some time θ, and $\Delta E/\Delta\theta$ is the average rate for some time interval $\Delta\theta$. If θ is the mid-point of the interval, $\Delta E/\Delta\theta$ will represent this mid-point rate quite closely. (Again, more elegant mathematical approaches are possible and may be necessary in some cases.) From the table prepared during the calculations, ΔE and ΔC are available for 1-hr intervals. Thus, for the 2- to 3-hr period,

$$\Delta E = 2064 \text{ lb}$$
$$\Delta C = 2376 \text{ lb}$$

We may then say, with reasonable accuracy, that, at 2.5 hr,

$$\frac{dE}{d\theta} = \frac{2064 \text{ lb}}{\text{hr}}$$

and $$\frac{dC}{d\theta} = \frac{2376 \text{ lb}}{\text{hr}}$$

A problem such as this is of real importance to the engineer evaluating the performance of a unit. A study of rates vs. time, plus a knowledge of the length of time necessary to clean the evaporator and of the tolerances allowed in composition, would help him to decide how often the unit should be cleaned, the type of operating records that should be kept, and the type and location of automatic control instruments.

With a small amount of additional information, we could determine the efficiency with which heat from the steam is being used or the minimum steam input required.

Example 5-6. In addition to the data and results of Example 5-5, information on total steam input is known. The feed has a heat capacity of 0.98 Btu/(lb)(F°). The feed enters at 67°F. The average boiling point in the evaporator is 215°F. The heat of vaporization is the same as that of pure water. The steam condenses at 242°F. Only the heat of vaporization of the steam is obtained; i.e., the condensed steam does not cool to give off further heat. Calculate the percentage of the heat, given off by the steam, that is used to heat the feed and vaporize water. (The rest is presumed lost through the insulation on the evaporator.)

Time, hr	0	1	2	3	4	5
Total steam used, lb	0	3610	7100	10,320	13,170	15,510

Solution. We shall tabulate the answers on an hourly basis. During any one hour, the feed is ΔF lb, the evaporate is ΔE lb, and the steam used is ΔS lb. Using as an example the period from 2 to 3 hr,

$$\Delta F = 4370 \text{ lb} \qquad \text{and} \qquad \Delta E = 2064 \text{ lb (from Example 5-5)}$$
$$\Delta S = 10{,}320 - 7100 = 3220 \text{ lb}$$

The heat used to heat the feed is

$$\Delta F\, \bar{c}_{p_F}(t_F - t_b) = (4370)(0.98)(215 - 67) = 634{,}000 \text{ Btu}$$

The heat used to vaporize the evaporate is

$$\Delta E\, \Delta H_v = (2064)(968.3) = 2{,}000{,}000 \text{ Btu}$$

where $\Delta H_v = 968.3$ Btu/lb, found from the table of properties of steam. Thus the total heat actually used is 2,634,000 Btu.

The heat which is given up by the steam is

$$\Delta S\, \Delta H_S = (3220)(950) = 3{,}060{,}000$$

where $\Delta H_S = 950$ Btu/lb is also found in the steam table.

The percentage of the heat used to heat and concentrate the solution is then

$$\left(\frac{2{,}634{,}000}{3{,}060{,}000}\right)(100) = 86\%$$

Therefore 14% of the heat given up by the steam is lost. We may make the entire calculation in tabular form.

Time period, hr	$(948)(0.98)\ \Delta F = 145\ \Delta F$	$968.3\ \Delta E$	$145\ \Delta F + 968.3\ \Delta E$	$950\ \Delta S$	$\frac{145\ \Delta F + 968.3\ \Delta E}{950\ \Delta S} \times 100 =$ % of heat used
0–1	715,000	2,370,000	3,085,000	3,430,000	90
1–2	684,000	2,235,000	2,919,000	3,315,000	88
2–3	634,000	2,000,000	2,634,000	3,060,000	86
3–4	566,000	1,680,000	2,246,000	2,705,000	83
4–5	483,000	1,269,000	1,752,000	2,220,000	79

Condensable-vapor Operations. Frequently in chemical processing it becomes necessary to handle mixtures of a condensable vapor and a noncondensable gas. The most common mixture is air and water vapor, which must be handled in air conditioning, drying of wet solids, and water cooling. For this reason the operations of humidification and dehumidification are commonly studied in chemical engineering. However, the subject is much broader in scope. It is very common to have to dry a solid which contains a liquid other than water or to remove vapors from streams consisting of these vapors in noncondensable gases. Often the gases are inert, such as nitrogen or carbon dioxide, because of the explosive dangers when the vapors (usually organic) are mixed with air.

Most problems in this field are solved rather easily by the use of the numerous "humidity" charts which are available. It is our purpose here to explore the background of these charts, which are based on material and energy balances, to learn the definitions commonly used, and finally to solve some problems using the charts. Again we must emphasize that the equations to be derived and the charts made from them are based on material and energy balances only; thus we are in no position to discuss the actual rates at which processes occur, and therefore we can make no calculations regarding the size of equipment. Numerous assumptions will be necessary as we progress in this discussion. At the start we mention two assumptions which will be applied to all cases:

1. The perfect-gas laws apply to the gaseous mixture.

2. The gaseous mixture may consist of any number of chemical compounds; only one of these is condensable. (Actually all gases can be condensed under proper conditions. The term "condensable" then refers to the component which can condense under the normally encountered conditions to which the mixture may be subjected.)

Let us consider first a general steady-state situation. We will let A refer to the pounds of a noncondensable gas (or mixture of noncondensable gases) and W refer to the condensable vapor. Let subscript 1 refer to inlet conditions and 2 to outlet conditions. Some noncondensable gas

containing some condensable vapor enters a piece of equipment. At the same time some liquid enters. Liquid and vapor-gas mixture also leave. Let t refer to temperature. The situation is shown in Fig. 5-2.

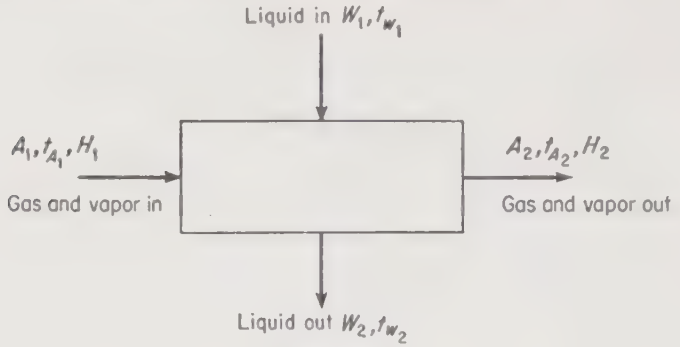


FIG. 5-2

Note on the diagram that the letter H has been used. This stands for "humidity," or "absolute humidity," and is defined as pounds of condensable vapor per pound of dry noncondensable gas. This definition is the most convenient for mixtures of this type. Note that this is not a weight fraction but a weight ratio. Note also that the definition is in terms of weights rather than the more fundamental moles. (We have previously used H to represent enthalpy. Unfortunately, H is used in both ways; consequently, in this section, we shall use h for enthalpy and H for humidity.)

We may immediately write the material-balance expressions for this system. Since we have defined it as steady-state, we may take any convenient time basis. Then let A refer to pounds of dry noncondensable gas per unit time and W to pounds of liquid during the same time interval.

Noncondensable gas: $A_1 = A_2$
Condensable vapor in

$$(A_1 \text{ lb dry gas}) \left(H_1 \frac{\text{lb vapor}}{\text{lb dry gas}} \right)$$

Condensable vapor out $= A_2H_2 = A_1H_2$

Balance on condensable material:

$$A_1H_1 + W_1 = A_1H_2 + W_2$$
$$W_2 - W_1 = A_1(H_1 - H_2)$$

This equation is perfectly general for the steady-state case. It applies to co-, counter-, and cross-current contact. It is valid for both humidification and dehumidification. Thus, if the gas is being dehumidified, H_1 is greater than H_2, and some of the condensable material is condensed. This

must show up as an increase in amount of liquid, that is, W_2 is greater than W_1. Conversely, in humidification, H_2 exceeds H_1, and thus W_1 must be greater than W_2.

Note the advantage of using weight ratios. Since the noncondensable gas passes through the process unchanged, it acts as a key component in the calculations. The simple product of A and H gives immediately the amount of condensable vapor carried along with the gas.

From our previous study of the properties of vapor-gas mixtures we know that there is a limit to the amount of vapor which can be contained in a given amount of gas. This limit is determined by the vapor pressure of the condensable material, which is a function of the temperature, and by the total pressure. Thus, while our equation

$$W_2 - W_1 = A_1(H_1 - H_2)$$

is mathematically correct under any assumed situation, it has physical meaning for only limited regions. We can represent this graphically very easily.

For purposes of establishing this relationship, assume the following:

P = total pressure
p_0 = vapor pressure of condensable material
M_A = molecular weight of gas
M_W = molecular weight of condensable material

Since the perfect-gas law applies,

$$\frac{n_W}{n_A} = \frac{p_W}{p_A}$$

where n = moles and p = partial pressure.
If m = weight of substance,

$$n = \frac{m}{M}$$

Also
$$p_A = P - p_W$$

and
$$\frac{m_W/M_W}{m_A/M_A} = \frac{p_W}{P - p_W}$$

or
$$\frac{m_W}{m_A} = \left(\frac{p_W}{P - p_W}\right)\left(\frac{M_W}{M_A}\right)$$

On a basis of $m_A = 1$, the ratio m_W/m_A has the units lb vapor/lb dry gas and is equal to the humidity H.

Thus,
$$H = \left(\frac{p_W}{P - p_W}\right)\left(\frac{M_W}{M_A}\right)$$

If the gas is saturated, then $p_W = p_0$, and

$$H_S = \left(\frac{p_0}{P - p_0}\right)\left(\frac{M_W}{M_A}\right)$$

where H_S = saturation humidity.

We see that the humidity and the saturation humidity are functions of the materials, the temperature, and the total pressure. All must be specified before the humidity can be determined.

Example 5-7. Compare the saturation-humidity values for the following cases.

	Total pressure, atm	Temp, °F	Gas	Vapor
a	1	70	Air	CCl_4
b	1	100	Air	CCl_4
c	1	70	CO_2	CCl_4
d	½	70	Air	CCl_4
e	1	70	Air	Water
f	1	170.1	Air	CCl_4

The following vapor pressures for CCl_4 are known.

t, °F	70	100	170.1
p_0, mm Hg	92	197	760

The vapor pressure of water at 70°F is 18.78 mm Hg.

Solution. In all cases the solution is a direct substitution in the formula

$$H_S = \left(\frac{p_0}{P - p_0}\right)\left(\frac{M_W}{M_A}\right)$$

a. $H_S = \left(\frac{92}{760 - 92}\right)\left(\frac{153.84}{28.9}\right) = \frac{0.732 \text{ lb } CCl_4}{\text{lb air}}$

b. $H_S = \left(\frac{197}{760 - 197}\right)\left(\frac{153.84}{28.9}\right) = \frac{1.86 \text{ lb } CCl_4}{\text{lb air}}$

c. $H_S = \left(\frac{92}{760 - 92}\right)\left(\frac{153.84}{44.01}\right) = \frac{0.481 \text{ lb } CCl_4}{\text{lb } CO_2}$

d. $H_S = \left(\frac{92}{380 - 92}\right)\left(\frac{153.84}{28.9}\right) = \frac{1.70 \text{ lb } CCl_4}{\text{lb air}}$

e. $H_S = \left(\frac{18.78}{760 - 18.78}\right)\left(\frac{18}{28.9}\right) = \frac{0.01575 \text{ lb } H_2O}{\text{lb air}}$

f. $H_S = \left(\frac{760}{760 - 760}\right)\left(\frac{153.84}{28.9}\right) = \infty$

The answers in the example illustrate that the saturation humidity depends on the substances, the total pressure, and the temperature. The answer to part *f* indicates also that there is no upper numerical limit to humidity. If a mixture of air and CCl_4 were saturated at a total pressure of 760 mm Hg and 170.1°F, the partial pressure of the CCl_4 would have to be equal to the total pressure. Thus, no air could be present. This accounts for the infinite value of the humidity.

We are now in a position to establish a curve representing saturation humidity as a function of temperature.

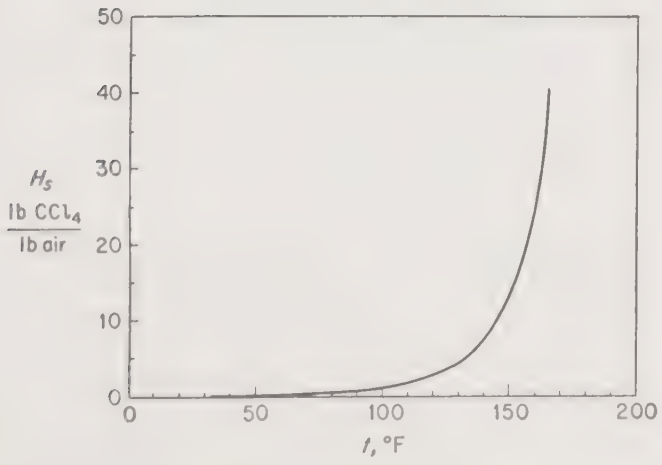
Example 5-8. Plot saturation humidity vs. temperature for the system CCl_4-air at a total pressure of 1 atm.

Solution. We need only to solve the equation

$$H_S = \left(\frac{p_0}{760 - p_0}\right)\left(\frac{153.84}{28.9}\right)$$

for enough points to establish a curve. Values of p_0 as a function of temperature are given in Appendix D. From a smooth curve of p_0 vs. t, the following points in the curve were established:

t, °F	p_0, mm Hg	H_S
40	42	0.311
80	123	1.026
120	295	3.375
140	430	6.93
160	635	27.0
170	760	∞



The results of the cal ulations are shown in the plot of humidity vs. temperature. Any point on the curve represents saturation conditions. It is impossible for a mixture to exist in the region above the curve. Such a mixture would be supersaturated with vapor, and some of the vapor would condense out. It is possible to have any condition falling to the right of the curve or below the curve. Any condition in this region is referred to as "unsaturated."

If we divide the equation for absolute humidity H by the equation for saturation humidity H_S, we obtain

$$\frac{H}{H_S} = \left(\frac{p_W}{p_0}\right)\left(\frac{P - p_0}{P - p_W}\right)$$

Multiplying the value of H/H_S by 100 we have the expression for the per cent absolute humidity.

It is possible to place lines of constant per cent absolute humidity on the diagram also. The method of calculation is shown in Example 5-9.

Example 5-9. Plot lines of 25 and 50% absolute humidity on a diagram of H vs. t for CCl_4-air mixtures for a total pressure of 1 atm. Determine also the partial pressures of CCl_4 in the mixture.

Solution. Values of H/H_S are easily obtained from known H_S values. Thus, for 50% humidity,

$$H = 0.5H_S$$

To find p_W, we must solve for p_W in the equation

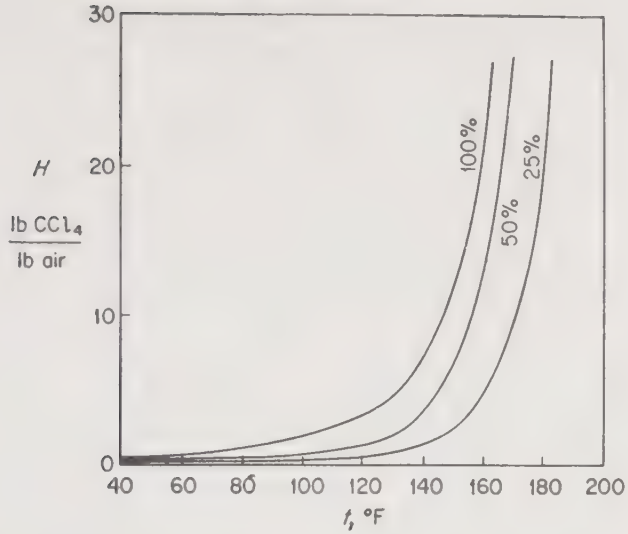
$$\frac{H}{H_S} = \left(\frac{p_W}{p_0}\right)\left(\frac{P - p_0}{P - p_W}\right)$$

Thus,

$$p_W = \frac{P}{(H_S/H)[(P - p_0)/p_0] + 1}$$

The solution is best done in tabular form.

t	H_S	p_0	$\frac{H}{H_S} = 0.25$		$\frac{H}{H_S} = 0.50$	
			H	p_W	H	p_W
40	0.311	42	0.078	10.95	0.155	21.6
80	1.026	123	0.257	35.0	0.513	67.0
120	3.375	295	0.844	104.0	1.688	183.0
140	6.93	430	1.73	186.5	3.47	300
160	27.0	635	6.75	425	13.5	545
170.1	∞	760	∞	(760)	∞	(760)



The results of the calculations of Example 5-9 are shown in the figure. Since the term $P - p_W$ appears in the denominator of the expression for per cent absolute humidity, all the curves of per cent absolute humidity vs. temperature approach infinity at the temperature at which the vapor pressure of the condensable gas is equal to the total pressure of the mixture (170.1°F in the example).

Another common term used in humidification work is *relative humidity*. This is defined by the equation

$$RH = \frac{p_W}{p_0}$$

which states that the relative humidity is the ratio of the partial pressure of the condensable gas to the vapor pressure of the gas at the temperature of the mixture. Note also in comparing the equation for the per cent absolute humidity and the relative humidity that these differ by the ratio $(P - p_0)/(P - p_W)$, that is

$$\% \text{ Abs. humidity} = (\% \text{ rel. humidity}) \left(\frac{P - p_0}{P - p_W}\right)$$

Most humidity diagrams contain lines of constant relative humidity rather than lines of constant absolute humidity. The method of establishing these lines is shown in Example 5-10.

Example 5-10. Draw lines of constant 25, 50, and 100% relative humidity on a humidity diagram for the CCl_4-air system for a total pressure of 1 atm. For comparison, calculate also the per cent absolute humidity.

Solution. In order to place lines on the diagram, values of H and t must be known. We again use the equation

$$\frac{H}{H_S} = \left(\frac{p_W}{p_0}\right)\left(\frac{P - p_0}{P - p_W}\right)$$

t	H_S	$(100)\left(\frac{p_W}{p_0}\right) = 25$				$(100)\left(\frac{p_W}{p_0}\right) = 50$		
		p_0	p_W	$(100)(H/H_S)$	H	p_W	$(100)(H/H_S)$	H
40	0.311	42	10.5	24	0.076	21	48.6	0.151
80	1.026	123	30.8	21.9	0.227	61.5	45.6	0.468
120	3.375	295	73.8	17.0	0.571	147.5	38.0	1.281
140	6.93	430	107.5	12.6	0.877	215	30.3	2.10
160	27.0	635	158.8	5.2	1.455	317.5	14.1	3.81
170.1	∞	760	190	0	.....	380	0	

By this calculation all values of H for t less than 170.1°F can be calculated. At this point, however, H is indeterminate, and other equations must be used.

$$RH = \frac{p_W}{p_0}$$

and

$$H = \left(\frac{p_W}{P - p_W}\right)\left(\frac{M_W}{M_A}\right)$$

Thus

$$H = \left(\frac{p_0(RH)}{P - p_0(RH)}\right)\left(\frac{M_W}{M_A}\right)$$

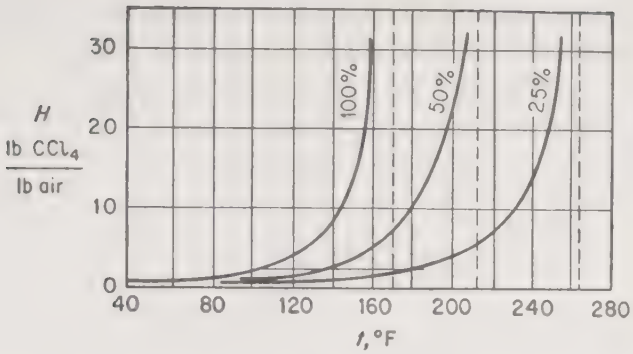
For example, for 140°F, $RH = 0.25$,

$$H = \left(\frac{(430)(0.25)}{760 - (430)(0.25)}\right)\left(\frac{153.84}{28.9}\right) = 0.877$$

which checks the previous value.

Using this equation, we continue the calculation. For $RH = 1.00$, H becomes infinite at 170.1. This is to be expected since the 100% RH and 100% H lines must be the same. Results of calculations for $RH = 0.25$ and 0.50 are shown in the table.

t, °F	p_0	$H(RH = 0.25)$	$H(RH = 0.50)$
170.1	760	1.77	5.32
200	1240	3.67	23.6
214.5	1520	5.32	∞
240	2016	10.5	
255	2620	33.2	
267	3040	∞	



The results of the calculations in Example 5-10 are shown in the figure. You will note that, in this case, the per-cent-relative-humidity lines do not all approach the same asymptote as do the lines for per cent absolute humidity. Instead, each line approaches infinity at a point where the term $P - p_0(RH)$ becomes zero, or where $p_0 = P/RH$.

A very important definition used in humidification work is the *dew point*. This point represents the temperature at which a given mixture of a condensable vapor and noncondensable gas would become saturated if this mixture were cooled at constant pressure and humidity. The path of such a process would represent a horizontal line going from the unsaturated region to the saturation curve.

Example 5-11. A mixture of CCl_4 and air at 180°F and a total pressure of 1 atm has a relative humidity of 25%. What are its humidity and dew point?

Solution. From the diagram of the previous example, the humidity is 2.5 lb CCl_4/lb dry air. If we follow a horizontal line to the saturation curve, the dew point is 110°F.

We may check the dew-point calculation as follows:

$$H = \left(\frac{p_w}{760 - p_w}\right)\left(\frac{153.84}{28.9}\right)$$

and $H = H_s$, $p = p_0$ on the saturation curve.

At 110°F, $p_0 = 242$ mm Hg. Then $H_s = 2.49$, which checks the value 2.50 read from the plot.

There are very important heat effects associated with condensable-vapor mixtures, and certain fundamental definitions arise from these heat effects. Let us consider the case where a gas (which may have some condensable vapor in it) is passed through a piece of equipment at a steady rate. In this equipment it is contacted with the liquid form of the condensable component, and some of the liquid evaporates. We will assume that the piece of equipment is of sufficient size that the gas-vapor mixture

leaving it is saturated with the condensable component. We will assume also that the liquid which is not evaporated is recirculated and that enough liquid is added to the recycle line to make up for that which is evaporated. Such a situation is shown in Fig. 5-3. We will assume also

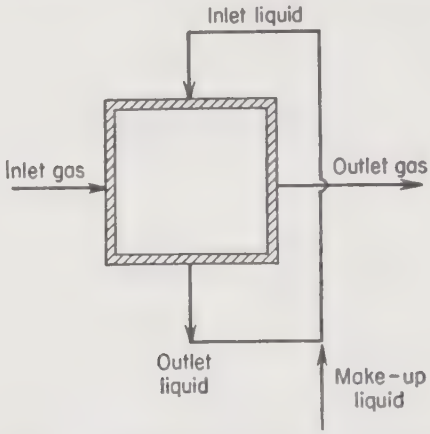


FIG. 5-3. Adiabatic saturation process.

that the piece of equipment in which the contact takes place contains no source of heat input and that there are no heat losses from the equipment.

Since this is a steady-state flow process with no accumulation or depletion of either material or energy within the equipment, we may make an enthalpy balance, based on A lb of noncondensable gas.

$$A[(1)\bar{C}_{p_A}(t_1 - t_b) + H_1\bar{C}_{p_W}(t_1 - t_b)] + W_1\bar{C}_{p_{W_1}}(t_{W_1} - t_b)$$
$$= A(H_2 - H_1)\Delta h_{vap,W} + A[\bar{C}_{p_A}(t_2 - t_b) + H_2C_{p_W}(t_2 - t_b)]$$

Suppose now that the outlet temperature of the gas t_2 is the same as the temperature of the liquid being passed through the apparatus. Suppose also that the temperature of the make-up liquid, t_{W_1}, is the same as the outlet temperature of the gas. Then choose $t_b = t_2$. We then see that all the heat necessary to vaporize the liquid comes from cooling the inlet gas-vapor mixture, i.e.,

$$(\bar{C}_{p_A} + H_1\bar{C}_{p_W})(t_1 - t_2) = (H_2 - H_1)\,\Delta h_{vap,W}$$

Under these circumstances the outlet temperature of this unit (equal to the temperature of the liquid being recycled) is defined as the *adiabatic saturation temperature*. This temperature is a unique property of the gas and liquid being used, of the total pressure, and of the inlet temperature and humidity of the vapor-gas mixture. Since it is an entirely defined quantity, it should be possible to place lines of constant adiabatic saturation temperature on a humidity diagram. The calculation of these lines is shown in the following examples.

Example 5-12. The following data for CCl_4 are known:

t, °F	C_p of liquid, Btu/(lb)(F°)	Δh of vaporization, Btu/lb
50	0.20	91.8
100	0.21	86.8
150	0.22	82.3
200	0.23	78.1
250	0.24	73.5
300	0.25	69.0

Vapor pressures are given in Examples 5-8 and 5-10.

The specific heat of air may be assumed constant at 0.24.

a. Calculate the adiabatic saturation temperature for dry air at 200°F.

b. Calculate the adiabatic saturation temperature for air with 1.5 lb CCl_4/lb dry air at 200°F.

c. What must be the humidity of air at 100°F if it has the same adiabatic saturation temperature as dry air at 200°F?

Solution

a. The formula

$$(\bar{C}_{p_A} + H_1\bar{C}_{p_W})(t_1 - t_2) = (H_2 - H_1)\,\Delta h_{vap,W}$$

is simplified in this case, since H_1 is zero. Inserting known values,

$$(0.24)(200 - t_2) = H_2\,\Delta h_{vap,W}$$

The solution now becomes trial and error. t_2 and H_2 must be consistent values from the saturation curve. $\Delta h_{vap,W}$ is the heat of vaporization at t_2.

Assumed t_2	$0.24(200 - t_2)$	H_2	$\Delta h_{vap,W}$	$H_2\,\Delta h_{vap,W}$
40	38.4	0.31	93	28.8
60	33.6	0.58	90.9	52.7
50	36.0	0.42	91.9	38.6
48	36.5	0.40	92.0	36.8

The last two values, 36.5 and 36.8, are in close agreement, indicating that the adiabatic saturation temperature is about 48°F, and the saturation humidity is 0.40.

b. In this case, the general formula cannot be simplified, since H_1 is not zero. Thus,

$$(0.24 + 1.5\bar{C}_{p_W})(200 - t_2) = (H_2 - 1.5)\,\Delta h_{vap,W}$$

The same relationships between t_2, H_2, and Δh apply as in part *a*. However, we also have the problem of establishing the correct value of $\bar{C}_{p_W}$ for

the CCl_4 vapor. This is the mean value between 200°F and the adiabatic saturation temperature. This is done by applying the principles of the thermodynamic path. Thus, to heat 1 lb of vapor from t_1 to t_2,

$$Q = \Delta h = \bar{C}_{p_V}(t_2 - t_1)$$

But, since $Q = \Delta h$, any other path would be satisfactory. Assume that we condense 1 lb at t_1.

$$Q_1 = -\Delta h_{vap} \qquad \text{at } t_1$$

Then we heat this pound of liquid from t_1 to t_2.

$$Q_2 = \bar{C}_{p_L}(t_2 - t_1)$$

Finally we vaporize this pound at t_2.

$$Q_3 = \Delta h_{vap} \qquad \text{at } t_2$$

Therefore,
$$\bar{C}_{p_V} = \bar{C}_{p_L} + \frac{\Delta h_2 - \Delta h_1}{t_2 - t_1}$$

Also, in this case, C_{p_L} is linear with temperature. Thus,

$$\bar{C}_{p_L} = C_{p_L} \text{ at } \frac{t_1 + t_2}{2} = t_{av}$$

With this information we may proceed with the problem. Again we assume t_2 and solve until the left and right sides of the equation give the same numerical value.

Assumed t_2	100	110	102
$\frac{t_1 + t_2}{2}$	150	155	
$\bar{C}_{p_L}$	0.22	0.221	0.22
$\Delta h_2 = \Delta h_{vap,W}$	86.8	85.8	86.7
Δh_1	78.1	78.1	
$\bar{C}_{p_V} = \bar{C}_{p_W}$	0.133	0.135	0.133
$(0.24 + 1.5\bar{C}_{p_V})(200 - t_2)$	44.0	39.8	43.1
H_2	1.8	2.49	1.95
$(H_2 - 1.5)\ \Delta h_2$	26.0	84.9	39.0

Without further calculation, the adiabatic saturation temperature may be estimated as 102.5°F. Further refinements are not justified, since H_2 was read from a plot in a steeply rising portion of the curve.

c. In this case the unknown quantity is H_1. Since t_1 and t_2 are known, all other quantities may be specified.

$$C_{p_W} = C_{p_V} = C_{p_L} \text{ at } t_{av} + \frac{\Delta h_2 - \Delta h_1}{t_2 - t_1}$$

$$t_1 = 100°\text{F} \qquad \Delta h_1 = \frac{86.8 \text{ Btu}}{\text{lb}}$$

$$t_2 = 48°\text{F} \qquad \Delta h_2 = \frac{92.0 \text{ Btu}}{\text{lb}}$$

$$t_{av} = 148/2 = 74°\text{F} \qquad C_{p_L} = 0.20$$

$$\bar{C}_{p_V} = 0.20 + \frac{92.0 - 86.8}{48 - 100} = 0.10$$

Thus the formula becomes

$$(0.24 + 0.10H_1)(100 - 48) = (0.40 - H_1)(92.0)$$

Solving, $H_1 = 0.25$ lb CCl_4/lb dry air.

Example 5-13. Plot lines of constant adiabatic saturation temperature on a humidity diagram for CCl_4-air at 1 atm total pressure. Show the calculations for 50, 75, and 100°F.

Solution. In all cases we are working from the formula

$$(\bar{C}_{p_A} + H_1\bar{C}_{p_W})(t_1 - t_2) = (H_2 - H_1)\,\Delta h_{vap,W}$$

For a given adiabatic saturation temperature the terms t_2, H_2, and $\Delta h_{vap,W}$ are known. $\bar{C}_{p_A}$ is assumed constant. Unknown terms are t_1, H_1, and $\bar{C}_{p_W}$. If we choose t_1, $\bar{C}_{p_W}$ may be determined, and the equation solved explicitly for H_1 by rearranging it to the form

$$H_1 = \frac{H_2\,\Delta h_{vap,W} - \bar{C}_{p_A}(t_1 - t_2)}{\Delta h_{vap,W} + \bar{C}_{p_W}(t_1 - t_2)}$$

For 50°F, $p_0 = 54$ mm Hg.

$$H_S = H_2 = \left(\frac{54}{760 - 54}\right)\left(\frac{153.84}{28.9}\right) = \frac{0.409 \text{ lb } CCl_4}{\text{lb dry air}}$$

$$\Delta h_{vap,W} = \frac{91.9 \text{ Btu}}{\text{lb } CCl_4}$$

$$H_2\,\Delta h_{vap,W} = \frac{37.7 \text{ Btu}}{\text{lb dry air}}$$

$$H_1 = \frac{37.7 - 0.24(t_1 - 50)}{91.9 + \bar{C}_{p_W}(t_1 - 50)}$$

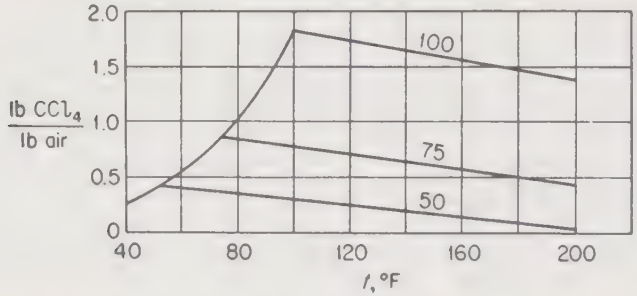
From Example 5-12,

$$\bar{C}_{p_W} = C_{p_L} \text{ at } t_{av} + \frac{\Delta h_2 - \Delta h_1}{t_2 - t_1} = C_{p_L} \text{ at } t_{av} + \frac{91.9 - \Delta h_1}{50 - t_1}$$

t_1	t_{av}	C_{p_L}	Δh_1	$\bar{C}_{p_W}$	H_1
100	75	0.205	86.8	0.103	0.265
150	100	0.210	82.3	0.114	0.133
200	125	0.215	78.1	0.123	0.015

Similarly, we may calculate curves for 75 and 100°F. The results are tabulated below:

Adiabatic saturation temperature, °F	75	100
p_0, mm Hg	107	197
$H_S = H_2$, lb CCl_4/lb dry air	0.872	1.86
$\Delta h_{vap,W}$	89.3	86.8
$\bar{C}_{p_W}$ to 100°F	0.108	
H_1 at 100°F	0.780	
$\bar{C}_{p_W}$ to 150°F	0.120	0.125
H_1 at 150°F	0.609	1.61
$\bar{C}_{p_W}$ to 200°F	0.128	0.133
H_1 at 200°F	0.455	1.37



The results of the calculation are shown in the diagram. If a piece of equipment is operating in the manner described above, it is possible, by use of the adiabatic-saturation-temperature lines, to plot the condition of the gas mixture at any point in the apparatus. This is true whether the gas leaves in a saturated condition or not.

You will note in the example that it is necessary to use the heat capacity of the gas-vapor mixture in order to solve the problem. If we group the heat capacities in the following manner

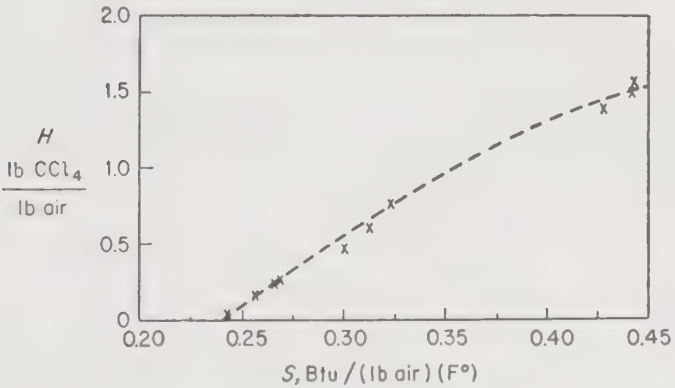
$$S = \bar{C}_{p_A} + H_1\bar{C}_{p_W}$$

we find that we have an equation which represents the heat capacity of 1 lb of dry gas plus whatever vapor it may contain. This grouping is commonly referred to as the *humid heat* of the mixture.

Example 5-14. From data in previous problems, calculate and plot S, humid heat, vs. humidity for the CCl_4-air system at 1 atm total pressure.

Solution. The following data and results are obtained:

Example	t_1	H_1	$\bar{C}_{p_W}$	t_2	S
12*a*	200	0	.....	48	0.240
12*b*	200	1.5	0.133	102	0.440
12*c*	100	0.25	0.100	48	0.265
13	100	0.265	0.103	50	0.267
13	150	0.133	0.114	50	0.255
13	200	0.015	0.123	50	0.242
13	100	0.780	0.108	75	0.324
13	150	0.609	0.120	75	0.313
13	200	0.455	0.128	75	0.298
13	150	1.61	0.125	100	0.441
13	200	1.37	0.133	100	0.422



The diagram shows the points, plotted as H vs. S. Note that the line is curved and that the points do not all fall on the curve. This is because of the fact that the heat capacity of CCl_4 is relatively sensitive to temperature, and, in the examples, various base temperatures, corresponding to adiabatic-saturation values, were chosen. Actually, most humidification diagrams show only a single line of H vs. S, when the C_p's are assumed independent of temperature in the limited temperature range considered. As long as H_1 is low, the error introduced is small. Also, the curve of H vs. S is straight under these conditions.

It is frequently necessary in making calculations on equipment for humidification or dehumidification to calculate volumes of material in and out of the unit. This, of course, is necessary to establish the proper size of the equipment. It is very easy to calculate the volume of a vapor-gas mixture because we are using the perfect-gas laws. When the gas laws are used, it is possible to plot a line for completely dry gas and a line for completely saturated gas. It is also possible to plot lines for various percentage humidities if these are desired. Such calculations are shown

in the following example. The volume of one pound of dry gas plus its accompanying vapor is referred to as the *humid volume* of the gas.

Example 5-15. Plot humid volume vs. temperature for (*a*) dry air, (*b*) saturated air, (*c*) air with 50% absolute humidity, and (*d*) air with 50% relative humidity for the CCl_4-air system at 1 atm total pressure.

Solution

a. For completely dry air, we rearrange the gas-law equation

$$V = \left(\frac{359}{28.9}\right)\left(\frac{t + 460}{492}\right)\frac{\text{ft}^3}{\text{lb}}$$

This is a linear equation, therefore we need to establish only two points and to connect them with a straight line:

$$t = 40°\text{F} \qquad V = 12.62$$
$$t = 200°\text{F} \qquad V = 16.66$$

b. For all conditions where CCl_4 is present, the total moles in the mixture, per pound of dry air, are

$$N = \frac{1}{28.9} + \frac{H}{153.84}$$

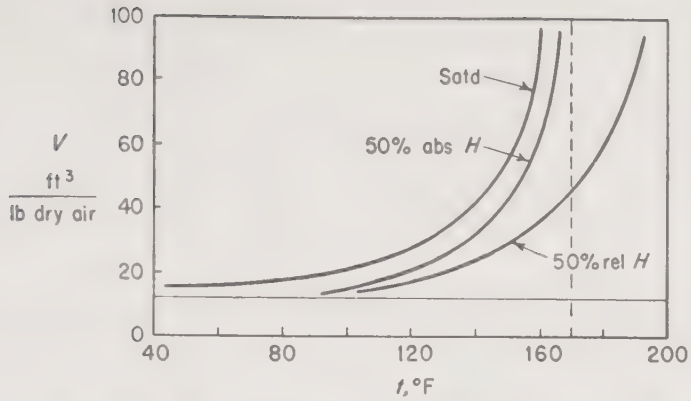
The humid volume is

$$V = (12.42 + 2.334H)\left(\frac{t + 460}{492}\right)\left(\frac{\text{ft}^3}{\text{lb dry air}}\right)$$

Parts *a* (with $H = 0$), *b*, *c*, and *d* can all be solved by this equation. Values are shown in the table. Humidities were previously obtained in Examples 5-8, 5-9, and 5-10

	Temperature, °F				
	40	80	120	160	200
a. $V(H = 0)$	12.62	13.64	14.64	15.65	16.66
b. H_s	0.311	1.026	3.375	27.0	*
V	13.36	16.27	23.93	95.05	*
c. H for 50% abs. hum.	0.155	0.513	1.688	13.5	*
V	12.99	14.95	19.29	55.35	*
d. H for 50% RH	0.151	0.468	1.281	3.81	23.6
V	12.98	14.84	18.17	26.85	90.59

* Values become infinite at 170.1°F.



The drawing shows the general nature of the curves. Note that the lines for saturated air and air with 50% absolute humidity approach infinity at the same asymptote, 170.1°F. The line for 50% relative humidity would approach infinity at an asymptote of 214.5°F.

Most humidity diagrams show lines for dry air and saturated air. Note that lines for a given percentage absolute humidity may be obtained by a weighted average of these lines. For example, at 50% absolute humidity and 160°F,

$$V = \frac{15.65 + 95.05}{2} = 55.35$$

This is *not* true for per cent relative-humidity values.

Note that all the quantities which we have defined so far, where they have a weight basis, have been based upon the use of 1 lb of dry material plus whatever additional material in the form of vapor may accompany this dry material. It is the easiest basis to use in problems of this type, since the noncondensable gas always passes through the process unchanged and may therefore be used very easily as a tie substance in calculations.

Another property of importance in humidification work is the *wet-bulb temperature*. To gain a physical picture, consider the following situation: A thermometer is fitted with a wick which is wet with the liquid form of the condensable component in the gas-vapor mixture. This so-called wet-bulb thermometer is placed in a stream of the mixture. It is assumed that the stream is large enough in quantity that its change in humidity and temperature is negligible. Because the stream is unsaturated, some of the liquid from the wick evaporates, thus cooling the thermometer. As soon as the thermometer starts to cool below the temperature of the gas-vapor mixture, heat is transferred from the mixture to the bulb. Eventually a steady-state situation is achieved where the rate of heat transfer to the thermometer is exactly counterbalanced by

the rate at which heat is used up to evaporate liquid from the wick. When this steady state is reached, the thermometer is at the wet-bulb temperature. (To avoid confusion, the actual gas-vapor-mixture temperature, which could be measured with a thermometer which is not fitted with a wick, is often called the *dry-bulb temperature.*)

Unfortunately it is not possible to present more theories of this subject here, because this phenomenon is dependent upon rate-of-heat and mass transfer. As such, it falls outside the scope of stoichiometry. However, it is essential that we point out that the wet-bulb temperature is also a unique property of the gas, the vapor, the total pressure, and the humidity of the mixture. Thus wet-bulb-temperature lines may be plotted on a humidification diagram. The usefulness of these lines is illustrated in later examples.

The discussion thus far has dealt with various aspects of condensable vapor-gas mixtures. Numerous terms have been defined and relationships established. Graphical representations of the terms have been shown. These may all be placed on one diagram, as shown in Fig. 5-4. By use of this diagram much time is saved in problem solution.

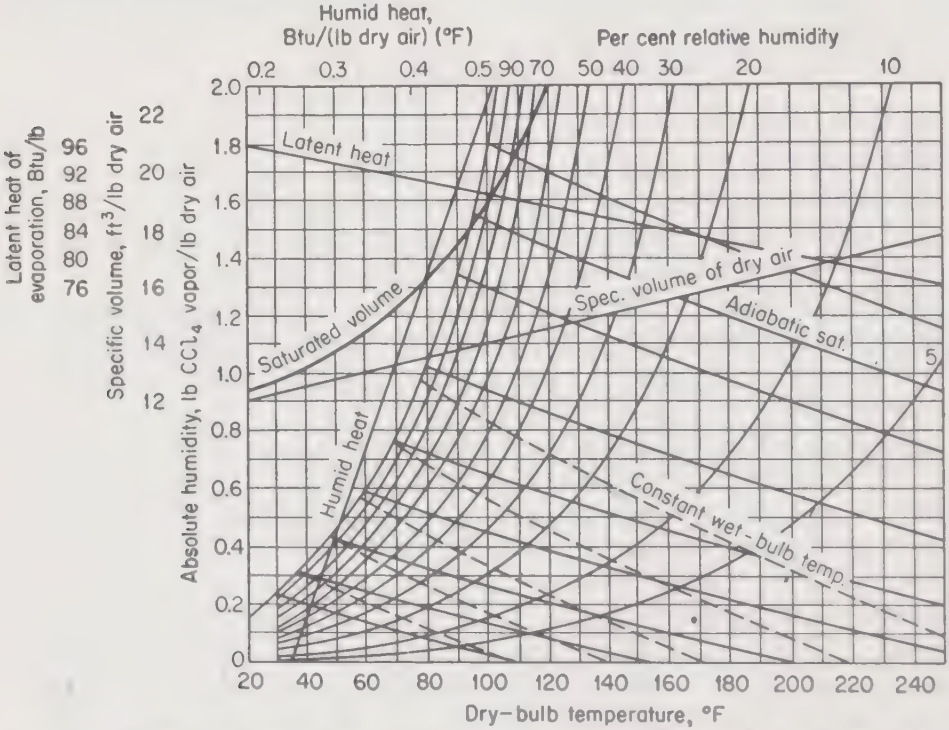

Humid heat, Btu/(lb dry air) (°F)
Per cent relative humidity
0.2 0.3 0.4 0.5 90 70 50 40 30 20 10
Latent heat of evaporation, Btu/lb
96 92 88 84 80 76
Specific volume, ft³/lb dry air
22 20 18 16 14 12
Absolute humidity, lb CCl4 vapor/lb dry air
2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0
Latent heat
Saturated volume
Spec. volume of dry air
Adiabatic sat.
Humid heat
Constant wet-bulb temp.
20 40 60 80 100 120 140 160 180 200 220 240
Dry-bulb temperature, °F

FIG. 5-4. Humidity chart for air-CCl_4 vapor mixtures. [*From J. H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., p. 813, McGraw-Hill Book Company, Inc., New York, 1950. Reproduced with permission of the publisher.*] *Note:* Latent heat of vaporization is plotted vs. temperature; humid heat is plotted vs. absolute humidity.

Example 5-16. A mixture of CCl_4 and air at 1 atm and 110°F has a humidity of 0.3 lb CCl_4/lb dry air. What items of information can be found on the humidity diagram?

The wet-bulb temperature is 60°F. A thermometer with a wick wet by CCl_4 and exposed to a moving stream of gas vapor under the above conditions would read 60°F. This value is obtained on the diagram by following a wet-bulb line to the saturation curve and reading the dry-bulb temperature corresponding to saturation.

The adiabatic saturation temperature is 54°F, and the adiabatic saturation humidity is 0.49 lb CCl_4/lb dry air. If the original mixture were blown through a chamber fed with liquid CCl_4 at 54°F and if it reached saturation, its outlet t and H would be 54 and 0.49, respectively. This is found on the diagram by following an adiabatic-humidification curve up to the saturation curve and reading the H, t coordinates of this point. If, in a piece of equipment, the air did not have time to become saturated, then the outlet condition would be a point on the adiabatic-humidification curve. $H = 0.44$, $t = 70$°F is such a point.

The dew point is 38°F. This is the point at which CCl_4 would begin to condense out if the original mixture were cooled at constant humidity and total pressure. This is obtained by reading the t coordinate for a saturation humidity of 0.3.

The relative humidity is about 18%. Thus the partial pressure of CCl_4 in the mixture is 18% of the vapor pressure at 110°F. This value is estimated by interpolating between the lines of constant per cent relative humidity.

The humid heat is about 0.29 Btu/(lb dry air)(F°). This is the heat necessary to raise the temperature of 1 lb of air plus 0.3 lb of CCl_4 1 F°. It is obtained by reading upward from the intersection of the line for $H = 0.3$ and the "humid heat vs. absolute humidity" line.

The latent heat of vaporization of CCl_4 at 110°F is 88 Btu/lb. The latent heat at the adiabatic saturation temperature is about 93 Btu/lb. These values are obtained by reading upward from the temperature of interest to the "latent heat of vaporization vs. temperature" line, then to the left.

The per cent absolute humidity cannot be determined from the diagram, since the line for saturation humidity runs off the chart before the temperature 110°F is reached. Since we cannot find this value, we cannot interpolate between the lines for specific volume of dry air and saturated volume to find the humid volume. These values would have to be calculated, knowing the vapor pressure at this temperature and using equations previously derived.

Appendix T is a humidity diagram for the system water vapor–air at a total pressure of 1 atm. Note that this looks much the same as the

diagram for CCl_4-air with one important exception. It has been found experimentally that the adiabatic saturation temperature and the wet-bulb temperature for this system are essentially the same. Thus one set of lines suffices for both. This is *not* a general rule. In the general case the adiabatic saturation temperature and the wet-bulb temperature are two entirely different things, both fundamentally and numerically.

Distillation. The final unit operation to be considered as a "case history" in this chapter is distillation. This is a process whereby mixtures of liquids are subjected to repeated partial vaporizations and condensations in order to separate them into more or less pure components. Practically every chemical plant will require some distillations in its processes; in the case of petroleum refining there is more distillation than any other operation.

In order for distillation to be useful, it is necessary for the liquid and vapor in equilibrium to have different compositions. If this is not the case, then some other process must be used.

A typical distillation column is shown in the Fig. 5-5.

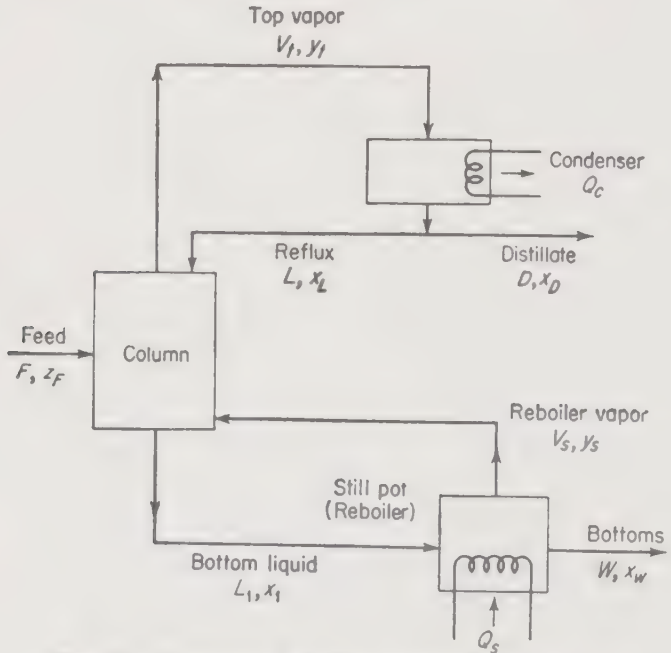


FIG. 5-5. Schematic diagram of distillation column.

The diagram shows feed F going into the column at some intermediate point. The top vapor is condensed, and the liquid stream of condensate is divided into the product, or distillate, D and reflux L. The bottom liquid is partially vaporized and is split into reboiler vapor V_s and

bottoms W. (The W is used because, in early work in the fermentation industries, the bottom product was "waste.")

The following nomenclature will be used:

F, D, W, L, and V = feed, distillate, bottoms, liquid, and vapor, respectively, lbmole/hr
x = mole fraction of liquid, subscript indicating stream
y = mole fraction of vapor, subscript indicating stream
z_F = mole fraction of feed

Note that it is customary in distillation to work with moles and mole fractions, whereas in evaporation we used weight fractions and in humidification we used weight ratios. Experience has shown that one method of handling concentrations may be quite well suited to one operation, while other methods are better for other operations.

In much distillation work binary mixtures (mixtures of two components) are handled. In such cases y (or x or z) is used for the more volatile component, and the mole fraction of the other is obtained by difference. In cases of multicomponent mixtures it is necessary to label each mole fraction carefully. In a ternary mixture, for example, we might call the most volatile component A, the next material B, and the least volatile one C. The distillate composition would then be expressed in terms of two mole fractions, say x_{D_A} and x_{D_B}, and then x_{D_C} would be obtained by difference.

The use of material and heat balances in the case of distillation is no different in principle from the use of these balances in any other operation. Actual calculation details may differ; again this is a matter of expediency and is in no way based on different principles. Restricting our discussion for the moment to binary mixtures, we may write these balances:

Total material: $$F = D + W$$

More-volatile component:

$$Fz_F = Dx_D + Wx_W$$

Less-volatile component:

$$F(1 - z_F) = D(1 - x_D) + W(1 - x_W)$$

Enthalpy: $$FH_F + Q_s = DH_D + WH_W + Q_c$$

Note that these equations are written for steady-state operation. Thus it is permissible to use an enthalpy balance for the heat balance. Note also that the total material and the two component balances are not

independent. Only two of the three equations are independent; the third may occasionally be used for checking arithmetic work.

In these equations the following new symbols have been used:

H = enthalpy, Btu/lbmole, with subscript indicating stream
Q_s = heat into still pot, Btu/hr
Q_c = heat removed from condenser, Btu/hr

Actually, Q_c should be indicated as going toward the system, in keeping with previous thermodynamic definitions, in which case it would always be negative. The usual practice is to make it positive, so that it indicates heat removed.

If the heat into the still pot is furnished by condensing steam, as is usually the case, then

$$Q_s = S\,\Delta H_S$$

exactly as in evaporation. If the heat is removed in the condenser by cooling water, flowing at the rate of w lb/hr, then

$$Q_c = (w)(1)(t_2 - t_1)$$

When we consider the condenser and reboiler, we find that we may write similar material and heat balances. Thus, around the condenser

$$V_t = L + D \qquad (t \text{ indicates "top"})$$
$$V_t y_t = L x_L + D x_D$$

and

$$V_t H_t = L H_L + D H_D + Q_c$$

(Actually, it is customary to use H for vapor enthalpies and h for liquid enthalpies. In a chapter where other unit operations using these symbols for different things have been discussed, it is difficult to avoid double use of symbols.)

Around the reboiler

$$L_1 = V_s + W$$
$$L_1 x_1 = V_s y_s + W x_W$$

and

$$Q_s + L_1 H_1 = V_s H_s + W H_W$$

In the case of the condenser, it is customary to use a *total condenser*. Thus, $x_D = y_t = x_L$. In the reboiler, however, the vapor returned to the column is definitely of a different composition from the liquid bottoms. In such a case it is necessary to have equilibrium data to make calculations.

If feed and outlet compositions in distillation columns are known, material balances are quite simple. Heat balances are a bit more difficult, if all the possible complications are to be considered. It is not our purpose here to delve into these complications, since they require extensive study of thermodynamics. We can explore some simpler cases,

however, which are representative of the majority of distillation cases to be considered. And we may safely use the relationships which we derive, if we are careful to restrict our work to fairly "ideal" cases. Consider the following example:

Example 5-17. The feed to a distillation column consists of 10,000 lb/hr of a liquid containing 45%m benzene and 55%m toluene at 80°F. This is separated into a distillate of 99%m benzene and a bottoms of 1.5%m benzene. The distillate is condensed at 179°F in the condenser. After condensation, the liquid is cooled in the condenser to 170°F. The ΔH of condensation is 13,180 Btu/lbmole. The bottoms leave at 230°F. The ΔH of vaporization of the bottoms is 13,750 Btu/lbmole. The ratio of reflux returned to the column to the distillate removed is 8.1:1. Heat is furnished by steam condensing at 270°F. Heat is removed by cooling water which rises in temperature from 70 to 120°F. In the reboiler the vapor returned to the column is 3.64%m benzene.

The heat capacity of all the liquid streams may be assumed to be 38 Btu/(lbmole)(F°). Calculate the following:

a. The moles of distillate and bottoms per hour
b. The moles of reflux and top vapor per hour
c. The moles of bottom liquid and reboiler vapor per hour
d. The pounds of steam and cooling water per hour

Solution. We first must find the moles of feed. On the basis of 1 mole of feed, we have

$$M_{av} = (0.45)(78) + (0.55)(92) = \frac{85.7 \text{ lb}}{\text{lbmole}}$$

$$\frac{10{,}000 \text{ lb/hr}}{85.7 \text{ lb/lbmole}} = \frac{116.7 \text{ lbmole}}{\text{hr}}$$

a. By material balance around the entire column, on the basis of 1 hr,

$$F = 116.7 = D + W$$
$$Fz_F = (116.7)(0.45) = (D)(0.99) + (W)(0.015)$$

From these equations, $D = 52.1$ lbmole/hr and $W = 64.6$ lbmole/hr.

b. By material balance around the condenser

$$L = 8.1D = \frac{422.0 \text{ lbmole}}{\text{hr}}$$

$$V_1 = L + D = \frac{474.1 \text{ lbmole}}{\text{hr}}$$

c. By material balance around the reboiler

$$L_1 = V_s + W = V_s + 64.6$$
$$L_1x_1 = (V_s)(0.0364) + (64.6)(0.015)$$

In this case we have three unknowns, V_s, L_1, and x_1, and so we must make use of a heat balance to complete the solution. For the entire column,

Heat in: $$FC_{pF}(t_F - t_b) + Q_s$$

where t_b = a base temperature.

Heat out: $$DC_{pD}(t_D - t_b) + WC_{pW}(t_W - t_b) + Q_c$$

Assume that $t_b = t_F = 80°F$. We know all values except Q_s and Q_c. But

$$Q_c = V_t[13{,}180 + (38)(179 - 170)] = 13{,}522V_t$$

$$Q_s = (52.1)(38)(170 - 80) + (64.6)(38)(230 - 80) + (13{,}522)(474.1)$$

$$Q_s = \frac{6{,}971{,}400 \text{ Btu}}{\text{hr}}$$

$$V_s = \frac{6{,}971{,}400}{13{,}750} = \frac{507.0 \text{ lbmole}}{\text{hr}}$$

(This assumes that all of Q_s goes to vaporize V_s, that is, that the amount of sensible heat into L_1 is negligible.)

$$L_1 = \frac{571.6 \text{ lbmole}}{\text{hr}}$$

and $$x_1 = 0.0340$$

d. For steam condensing at 270°F, $\Delta H_{vap} = 931.8$ Btu/lb.

$$\frac{6{,}971{,}400}{931.8} = \frac{7482 \text{ lb steam}}{\text{hr}}$$

For the condenser

$$w = \frac{Q_c}{\Delta t} = \frac{13{,}522V_t}{120 - 70} = \frac{128{,}220 \text{ lb } H_2O}{\text{hr}}$$

The important thing to note about this problem is that it was solved, not because of a knowledge of distillation, but because the principles of material and heat balances were applicable, just as in operations studied previously. Note also that, again, we have made no comments about the actual appearance or arrangement of the equipment. That this column would require something between 15 and 30 "theoretical stages" and might be 20 to 50 ft high is extremely important but is not to be deduced from material and heat balances alone.

It is also interesting to note that the problem as formulated is feasible for the benzene-toluene mixture. It would be equally easy to solve the material-balance relationships, had the mixture supplied been ethanol-water. Furthermore, if heat-capacity and enthalpy-of-vaporization data had been available for ethanol-water, it would have been possible to

calculate the amounts of steam and cooling water needed. However, the answers would have been impossible, because the ethanol-water mixture cannot be separated into these compositions by ordinary distillation. Only a knowledge of the vapor-liquid equilibrium relationship for this mixture would have saved you from making an impossible, and therefore ridiculous, set of calculations. For reasons such as these, we must again emphasize that material and energy balances are perfectly valid, assuming that the postulated separation (or other physical or chemical change) is possible.

SUMMARY

We have attempted to describe the unit-operations concept because it is at present the basis of all chemical-engineering education and practice. We have presented some case histories of unit operations as a vehicle for illustrating further the usefulness of material and heat balances. Certain important concepts, such as inventory change, have been introduced. In several places we have given warnings about how far you may expect to go on the basis of material and heat balances alone before you may encounter troubles.

The problems at the end of the chapter are designed to review some of the concepts using the unit operations which have been discussed extensively. In addition, there are numerous problems on operations which have not been mentioned at all. These can be approached with the same confidence as can the problems in evaporation, humidification, and distillation. No matter what the equipment looks like or what operation it performs, we can always say "rate of input—rate of output = rate of accumulation."

PROBLEMS

5-1. An experimental reactor is being run to crack propane by this reaction:

$$C_3H_8 \rightarrow C_3H_6 + H_2$$

Pure propane is fed at 25°C and 3 atm pressure at a rate of 10 ft/sec through a pipe of 3-in. ID. The gas is preheated, reacted, and the products cooled. The reaction is 50% completed; i.e., only 50% of the propane is cracked. The products leave at 25°C, 2 atm, through a 5-in. ID pipe. Calculate the following:

a. The mass rate into the reactor, lb/hr
b. The mass rate out
c. The molal rate in
d. The molal rate out
e. The net heat in or out
f. The outlet velocity

5-2. A solution contains 60 %w $Na_2S_2O_2$ and 1 % soluble impurity in water. Upon cooling to 10°C, $Na_2S_2O_2 \cdot 5H_2O$ crystallizes out. The solubility of this hydrate is 1.4 lb $Na_2S_2O_2 \cdot 5H_2O$/lb free water. The crystals removed carry as adhering solution

0.06 lb solution/lb crystals. These are dried to remove the remaining water (but not the water of hydration). The final dry $Na_2S_2O_2 \cdot 5H_2O$ crystals must not contain more than 0.1%w impurity. In order to meet this specification, the original solution, before cooling, is further diluted with water. On the basis of 100-lb original solution, calculate the following:

a. The amount of water added before cooling

b. The percentage recovery of the $Na_2S_2O_2$ in the crystals

5-3. A 3%w salt solution (3 lb salt/100 lb solution) is evaporated to 15% in a single-effect evaporator. The heat capacity of the entering 3% solution is 0.98 Btu/(lb)(F°); that of the 15% solution is 0.90. The feed temperature is 70°F. The boiling point in the evaporator is 220°F. It requires 970 Btu to evaporate 1 lb of water from the boiling solution. The steam gives up only its latent heat of vaporization, 946 Btu/lb.

a. How many pounds of steam are required per 100 lb of feed?

b. It is proposed to run the concentrated solution through a countercurrent heat exchanger (economizer) to heat the feed. If the concentrated solution is cooled in the economizer from 220 to 120°F:

(1) How much heat is transferred to the feed stream?

(2) What percentage decrease in steam consumption results?

5-4. An evaporator operating at steady state is concentrating 100 lb/min of a water solution containing 10%w NaOH and 0.1%w NaCl. While a storage tank is being repaired, the outlet concentrate is fed into another tank which already contains 2000 lb of a solution of pure NaOH in water. At the end of 1 hr the mixed solution in this tank contains 31.34%w NaOH and 0.171%w NaCl. Calculate the following:

a. The concentration of the 2000 lb originally in the tank

b. The composition of the concentrate from the evaporator

c. The pounds of water evaporated in 1 hr

5-5. An evaporator in a chemical plant is set up as follows: Fluid from a process is fed into a storage, or "buffer," tank. From this tank it is fed to the evaporator. From the evaporator the concentrate is fed to a storage tank. Because of irregularities in steam available for the evaporator, two control devices are used. The feed to the evaporator is controlled to maintain a constant level in the evaporator. Concentrate removal is controlled so that the concentration is constant. Also, because of the layout of equipment, it is the duty of one operator to keep records on the amount of liquid in the buffer tank. Another operator keeps the records on the amount of concentrate in the storage tank. The feed into the buffer tank is steady at 5000 lb/hr. During the last part of the night shift, with reliable workmen on duty, the following data are taken:

Time, A.M.	Lb in buffer tank	Lb in storage tank
4	10,000	2,000
5	9,000	5,000
6	9,000	7,500
7	8,500	10,250
8	9,500	12,250

During the day shift the operator recording the storage-tank data is accused of loafing and filling in the data sheet later. From the data taken during the day, is the accusation correct?

Time	Lb in buffer tank	Lb in storage tank
8	9,500	12,250
9	10,000	14,500
10	10,000	17,000
11	11,000	18,700
12	11,400	21,000
1 P.M.	11,600	23,700
2	11,400	26,000
3	10,600	29,200
4	10,000	32,000

5-6. Ten thousand pounds per hour of a 6%w solution of salt in water is fed to an evaporator. Saturated solution is produced, and some of the salt crystallizes out. The hot crystals, with some adhering solution, are centrifuged to remove some of the solution. Then the crystals are dried to remove the rest of the water. During a 1-hr test, 837.6 lb concentrated solution was removed, 198.7 lb solution was removed from the centrifuge, and 361.7 lb dry crystals were removed from the drier. Previous tests on the centrifuge show that it removed about 60% of the adhering solution. Calculate the following:

a. The solubility of the salt
b. The water evaporated in the evaporator
c. The water evaporated in the drier

5-7. A mixture of CCl_4 and air at 1 atm total pressure and 100°F has a relative humidity of 40%. This is cooled at constant pressure to 40°F. Calculate the following:

a. The CCl_4 condensed/lb dry air
b. The heat removed/lb dry air

5-8. One hundred cubic feet of a mixture of CCl_4 and air at 60°F, $H = 0.2$, is mixed with 400 ft^3 at 120°F with a relative humidity of 40%. The mixing takes place at a constant total pressure of 1 atm, without heat exchange with the surroundings, i.e. adiabatically. Using the humidity diagram and additional calculations where needed, calculate the following:

a. The moles of mixture
b. The mole fraction of CCl_4 in the mixture
c. The pounds of mixture
d. The final humidity
e. The final temperature
f. The final volume
g. The relative humidity
h. The dew point
i. The adiabatic saturation temperature
j. The wet-bulb temperature

5-9. In Perry's Handbook,* page 811, we find these equations for the air–water-vapor system:

For the specific volume of dry air

$$V_d = 11.57 + 0.025t$$

* John H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950.

For the humid volume of saturated air

$$V_s = (0.0405)(460 + t)(0.622 + H_s)$$

where V_d = specific volume, ft³/lb
V_s = humid volume, ft³/lb dry air
t = °F
H_s = saturation humidity, lb water vapor/lb dry air

Derive these equations.

5-10. Using vapor-pressure data, verify by calculation the saturation curve for air–water-vapor mixtures at 1 atm total pressure.

5-11. Verify by calculation one of the adiabatic-saturation lines for the air–water-vapor system at 1 atm.

5-12. Verify one of the constant-relative-humidity lines for air-water.

5-13. Verify the humid-heat, dry-volume, and saturated-volume lines for air-water.

5-14. One poundmole of methane, CH_4, is burned completely to CO_2 and water with 50% excess air. The dry-bulb temperature of the products is reduced to 100°F. What is the wet-bulb temperature? Does any water condense? The total pressure is 760 mm Hg.

5-15. A wet paper pulp is to be dried from 60 to 20%w H_2O. These values are on a wet basis; i.e., 60% means 0.6 lb H_2O/lb wet paper. Air at 110°F with a humidity H of 0.006 lb H_2O/lb dry air is to be used. The specific heat of this air may be assumed constant at 0.25 Btu/(lb dry air)(F°). During the drying the paper temperature does not change. Approximately 1060 Btu are required to vaporize and heat 1 lb of water under these conditions.

a. Per pound of dry paper, what is the minimum air which may be used if its outlet temperature is not allowed to fall below 80°F?

b. What is the outlet humidity of the air?

5-16. A solid is to be dried from 50%w to 10%w moisture (dry basis) in a continuous drier. Nine hundred pounds of wet solid will be fed to the drier per hour. The "fresh air" for the preheater is at 78°F and 60% relative humidity.

The following procedures are under consideration. Draw each on a rough humidity chart, labeling the points carefully, and answer the questions asked below.

a. Fresh-air consumption is 2970 ft³/min. Drying is adiabatic. Exit air (from the drier) is at its dew point. To what temperature must the fresh air be preheated?

b. Fresh-air consumption is 2970 ft³/min. Latent heat of vaporization is supplied by an internal heater. Exit-air relative humidity is 90%. To what temperature must the fresh air be preheated?

c. Fresh-air consumption is 2970 ft³/min. Drying is adiabatic. Fresh air is preheated to 180°F. What will be the percent relative humidity of the exit air?

d. Drying is adiabatic. Exit air is saturated. Fresh air is preheated to 200°F. What percentage decrease in the fresh-air feed is necessary?

5-17. A rotary drier is run in the following manner: Fresh air at 60°F dry-bulb and 45°F wet-bulb is mixed with recycled air, at 112°F dry-bulb and a dew point of 104.3°F, from the drier exit. This mixture is heated to 200°F dry-bulb, 88.5°F dew point, and enters the drier under these conditions. Fresh air is fed to the unit at the rate of 184,000 ft³/hr, based on actual fresh-air conditions. Sixteen hundred and fifty-seven pounds of wet solid, containing 39.7%w moisture on a wet basis, enters the drier each hour. The solid enters at 105°F and leaves, completely dry, at 175°F. The flow is countercurrent. Heat losses are negligible. Calculate the following:

a. The pounds of fresh dry air per hour

b. The pounds of dry air recycled per pound of fresh dry air
c, *d*. The pounds of water evaporated, by two methods
e. The heat capacity of the dry solid
f. The pounds of steam, condensing at 225°F, which must be condensed each hour in the air heater

5-18. In a spray drier a liquid solution of the material to be dried is sprayed into a stream of hot gas. The water evaporated from the solution leaves with the exit gases. The solid is recovered by means of cyclone separators. In one test the following data are taken:

Inlet air: 100,000 ft^3/hr, 600°F, 780 mm Hg, dew point 40°F
Inlet solution: 300 lb/hr, 15%w solids, 70°F
Outlet air: 200°F, 760 mm Hg, dew point 100°F
Outlet solid: 130°F

The outlet solid is not entirely dry. The heat capacity of dry solid is 0.2 Btu/(lb)(F°). Calculate the following:
a. The composition of the outlet solid
b. The Btu given up by the inlet gas
c. The Btu to heat the water and vaporize it
d. The Btu to heat the remaining outlet solid
e. The percentage of the heat given up by the gas that is lost as radiation

5-19. A mixture of 0.0783 lb benzene/lb nitrogen at 1 atm has a per cent absolute humidity of 48.6%. What is the per cent relative humidity?

5-20. In distillation work, compositions of liquid and vapor in equilibrium are often calculated by means of "K values,"
where $y = Kx$
y = mole fraction of particular component in vapor
x = mole fraction of same component in liquid
K is called the *equilibrium constant*.

a. A mixture of 10%m propane, C_3H_8; 48.4% *n*-butane, C_4H_{10}; and 41.6% *n*-pentane, C_5H_{12}, boils at 100°F at a total pressure of 3 atm. The K values are 2.7, 1.2, and 0.36, respectively, at these conditions. Calculate the composition of the vapor in equilibrium with the liquid.

b. The over-all composition of a mixture is 15%m propane, 50% *n*-butane, and 35% *n*-pentane. Calculate the relative amounts and compositions of liquid and vapor phases at equilibrium at 100°F and 3 atm, carefully working out the mathematical relationships that exist.

5-21. In the distillation problem used as an example (Example 5-17), the following data were given or calculated:

Feed: 10,000 lb/hr, $x = 0.45$ (mole fraction benzene in toluene)
Distillate: 52.1 lbmole/hr, $x = 0.99$
$L/D = 8.1/1$
Bottoms: 64.6 lbmole/hr, $x = 0.015$
Reboiler vapor: 507.0 lbmole/hr, $y = 0.0364$
Bottom liquid: 571.6 lbmole/hr, $x = 0.0340$

Calculate and tabulate weight fractions and weight rate of flow for feed, distillate, top vapor, reflux, bottoms, bottom vapor, and bottom liquid. Check the weight material balances.

5-22 A mixture of 50%m toluene and 50% ethylene dichloride is distilled continuously in a column, the bottom product being 95% toluene and the top product 98% ethylene dichloride. The bottom of the column contains a reboiler where the level may change. The liquid in this reboiler is of the bottoms composition. On the basis of 100 mole of feed, calculate the amounts of the two streams discharged during a period when there is an accumulation of 5 mole of material in the reboiler.

5-23. In a distillation column for separating phenol and water, if the feed is less than 1.68%m phenol, the top-vapor composition will not be greater than 1.92% phenol, because of the formation of an azeotrope (constant-boiling mixture). Upon condensation, if the average composition is between 1.68 and 1.92%, the top vapor separates into two layers (at 20°C). One layer, containing 1.68% phenol, is fed back to the column as reflux. The other, containing 33.1% phenol, is removed for further processing.

If 100 mole of a solution of 1% phenol and 99% water is fed to a column per hour, the bottoms contain 0.1% phenol, and the average top-vapor composition (before condensation) is 1.9%, how many moles are returned as reflux per hour?

5-24. In the distillation-problem example (Example 5-17), 116.7 lbmole/hr of a mixture of 45%m benzene in toluene was separated into a distillate of 99% benzene and a bottoms of 1.5% benzene. In the condenser 13,522 Btu were removed per mole of top vapor condensed. Thirteen thousand seven hundred and fifty Btu were supplied by the steam per mole of reboiler vapor. The distillate left at 170°F, the bottoms left at 230°F, and the feed was introduced at 80°F. It has been proposed to change operations by introducing the feed as saturated vapor at 210°F. [The heat capacity of the feed may also be assumed to be 38 Btu/(lbmole)(F°), and the heat of vaporization at 210°F is about 13,750 Btu/lbmole.] In order to get the same separation as before, it is estimated that the ratio of L/D at the top of the column must be increased from 8.1 to 10.0.

a. Calculate the per cent change in steam flow to the reboiler and cooling-water flow to the condenser.

In order to heat the feed and vaporize it, it is proposed to use three heat exchangers in series. The feed will be heated from 80 to 160°F by condensing some of the top vapor. Assuming that each mole of top vapor gives up 13,522 Btu, the same as in the water-cooled condenser,

b. How many moles of top vapor will be condensed?

In the second heat exchanger the feed at 160°F will be further heated by the hot bottoms. The feed temperature can be allowed to rise to within 5 F° of the exit temperature of the bottoms from this heat exchanger.

c. What is the exit temperature of the feed from this exchanger?

Finally, in the third exchanger, the feed will be heated to 210°F and vaporized by steam condensing at 270°F.

d. Comparing the total steam used in this case with that used in the example, is the operation economical?

5-25. One poundmole per minute of a dry gas mixture containing 60%m N_2 and 40% SO_3 is fed to the bottom of a countercurrent absorption tower. Fifty pounds of 60%w H_2SO_4 in water is fed to the top of the tower in the same time. The concentrated acid leaving the bottom contains 84.8% H_2SO_4. The exit gases leave the top of the tower at a total pressure of 29 in. Hg. Water vapor in the gases exerts a partial pressure of 7 in. Hg. What percentage of the entering SO_3 is absorbed and converted to H_2SO_4?

5-26. In a liquid-liquid extraction a solvent is fed into the bottom of a column countercurrent to a stream of liquid containing a solute. The leaving stream of

solute in solvent is called the *extract*, and the leaving stream of liquid which has been depleted is called the *raffinate*. The degree of extraction depends on the physical layout of the equipment, the relative quantities of materials, and the relative solubilities of the solute in the two liquids.

In a typical experiment a steady flow of 100 lb/hr of liquid A containing 5 lb of solute S (i.e., a total flow of 105 lb/hr) is fed into the top of a column. Pure solvent B is introduced at the bottom. The concentration of solute in the extract is such that it is in equilibrium with the entering solution (when this is possible), and this equilibrium is determined by a distribution coefficient

$$K = \frac{C_B}{C_A}$$

where C_A = lb solute/lb liquid A and C_B = lb solute/lb liquid B.

If $K = 2$, calculate the extract and raffinate compositions for flow rates of 25, 50, and 100 lb pure B/hr. What is the highest flow rate for B that could possibly be economical?

Chapter 6

CHEMICAL PROCESSES

The application of the concept of unit operations stimulated the development of chemical-engineering technology to a remarkable degree. Because of this concept, the field was developed by investigation of the connective principles of the physical-separation processes rather than by concentration on the discrete problems of each particular industry, and chemical engineering advanced from the stage of art to the stage of science. Attention was then turned to the numerous chemical reactions employed industrially in an effort to achieve a corresponding recognition and elucidation of their similarities. The chemical reactions (called *processes* to distinguish them from physical separations, which were called *operations*) were divided into unit processes. Professor R. N. Shreve* lists the principal unit processes as follows:

1. Combustion
2. Oxidation
3. Neutralization
4. Silicate formation
5. Causticization
6. Electrolysis
7. Double decomposition
8. Calcination
9. Nitration
10. Esterification
11. Reduction
12. Ammonolysis
13. Halogenation
14. Sulfonation
15. Hydrolysis
16. Hydrogenation
17. Alkylation

* "The Chemical Process Industries," McGraw-Hill Book Company, Inc., New York, 1945.

18. Friedel-Crafts
19. Condensation
20. Polymerization
21. Diazotization and coupling
22. Fermentation
23. Pyrolysis
24. Aromatization
25. Isomerization

Although reactions within a classification may show certain similarities in energy relationships, rates, etc., and may be carried out in similar equipment, an examination of the list of unit processes reveals many exceptions and disparities. For example, the nitration of naphthalene is more like the sulfonation of naphthalene than it is like the nitration of methane. The lack of fundamental similarities in each class of unit processes is apparent to such a degree that the concept is not nearly as useful as that of unit operations.

In this chapter, we shall consider a few typical chemical processes. They are representative of the broad field of industrial chemistry. It is not our aim to make you expert in the calculations of any one process but rather to show how the principles thus far developed are applied in practice. We have not simplified complex situations for use as illustrations. We have considered less complex, but genuine, situations. The calculations are typical sound industrial practice. You can build a firm foundation on them and can, if you ever need to, become more expert in a particular process by learning additional facts and techniques for refinement (rather than replacement) of these calculations.

Material balances have been discussed before heat balances in each instance because they are prepared first.

We have presented an integrated, verbal picture of each process before discussing details. The description emphasizes connective principles and helps you to understand why the calculation of certain quantities is stressed in the detailed discussions of parts of the process. The first two processes which we consider, combustion of fuels and oxidation of sulfur, are good examples of processes that are so widely employed that the calculations have been systematized in the engineering literature.

COMBUSTION

By far the most commonly employed industrial process for heat generation is called *combustion*, or *burning*. This is a chemical reaction (oxidation) in which one of the reactants is free (oxygen in air) and the other is relatively cheap (fuel gas, fuel oil, coal). When combustion is

practiced for commercial purposes it must be accomplished as economically as possible. The most important factors affecting economy are the efficiency of consumption of the combustible matter and the efficiency of transfer of the heat generated.

Consumption Efficiency. There are two causes of inefficient utilization of fuel. One is loss of some of the combustibles charged, and the other is incomplete or partial combustion of the combustibles burned.

The magnitude of these inefficiencies may be determined by analysis of the furnace refuse and combustion gases ("flue" gases). Since the final measure of any industrial process is its profitability, losses of both types are permitted so long as the cost of preventing them is higher than the value of the heat that would be saved. In the case of losses in the refuse, different types of coal and/or furnaces are considered. In the case of loss of potential heat by partial oxidation (carbon to CO rather than to CO_2), the decision is influenced by considerations of heat-transfer efficiency as indicated in the following section.

Heat-transfer Efficiency. Heat-transfer efficiency depends upon the temperature level at which heat is available and upon the mechanical design of the heat-exchange apparatus. The temperature of the flue gases depends upon the nature of the fuel and upon the amount of air used for combustion. In order to promote efficient consumption of the fuel, excess air is used, but the greater the excess, the lower the flame temperature and the poorer the heat-transfer efficiency. Therefore, to select an optimum air-fuel ratio, a balance between fuel economy and heat-transfer economy must be made. The design of heat-exchange apparatus is beyond the scope of this book. Our calculations will be confined to heat balances around existing equipment.

In the preceding paragraphs we have discussed "consumption efficiency" and "heat-transfer" efficiency. These are the things which really matter in furnace performance, but it is not common industrial practice to discuss them in this manner. Since the purpose of furnace operation is to raise heat, all inefficiencies are discussed in industry from the standpoint of the heat loss which they represent. In the case of heat losses accruing in transfer of the generated heat (such as loss in furnace gases because their temperature level was too low or loss to surroundings because of poor insulation), we are considering real heat quantities. In the case of losses by discharge of partially oxidized or unburned combustibles, we are considering quantities of heat that could have been generated but were not. We say that these are losses of "potential" heat, or "heating value."

In the succeeding discussion of reactants, refuse, and flue gases, the details of energy and material flow are examined.

Figure 6-1 is a diagrammatic representation of a furnace showing the

entering and leaving streams. The elemental constituents of each stream are indicated. Before we consider the measurement and/or analysis of individual streams in detail, let us consider the integral process, emphasizing those factors which are primary from the standpoint of material

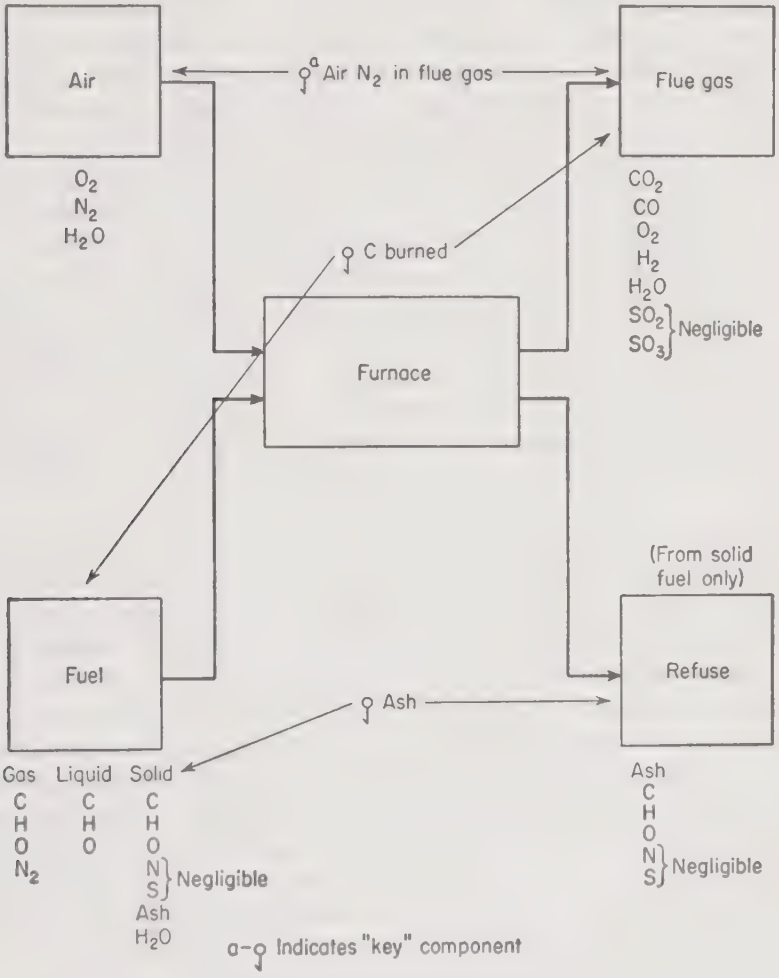


FIG. 6-1. Furnace streams.

balance. Since the primary task in preparing a material balance is to develop the quantitative relationships between the streams (rather than within them), the primary factors which we must consider are those which "tie" the streams together. Remember that we should not choose a basis arbitrarily. Our choice of basis may simplify or complicate the calculations, but it in no sense "permits" or "forbids" a solution. The recognition of the fact that certain quantities of elements or compounds

may be used to determine equivalent stream quantities is what leads to a problem solution. We have called the primary factors *key* components.

The key component relating a solid fuel and the furnace refuse is the ash. This is the material which cannot be gasified. (The term "gasified" means "changed to a gas or vapor." Water is simply vaporized; carbon is changed to the monoxide or dioxide.) Note the emphasis on the word "cannot." An individual furnace may not gasify all gasifiable material in the fuel charged to it. The ash contents of both the coal and the refuse are determined by an analytical procedure that effects total possible gasification. All the ash in the coal leaves the furnace in the refuse. Therefore a quantity of coal containing a specific amount of ash is equivalent to a quantity of refuse containing the same amount of ash. Gaseous and liquid fuels contain no ash and produce no refuse.

The key component relating the flue gas and fuel is the carbon gasified. Some of the carbon charged in solid fuels is unburned (ungasified) and leaves with the refuse. An ash balance and refuse analysis are necessary to determine the fraction of carbon charged that is unburned. Since all the carbon gasified appears in the flue gas, equivalent quantities of flue gas and fuel may be calculated when the amount of carbon gasified is known.

The key component relating the flue gas and air is the "air nitrogen." All the nitrogen entering with the combustion air appears in the flue gas. Nitrogen entering in the fuel also appears in the flue gas. The quantity of nitrogen in solid and liquid fuels is negligible, and it is possible to determine equivalent quantities of air and flue gas simply by calculating, with the aid of the flue-gas analysis, the amounts of air and flue gas which contain equal quantities of nitrogen. The quantity of nitrogen in gaseous fuels, however, is appreciable and must be accounted for in the determination of air nitrogen. The fuel-gas analysis, giving the carbon-nitrogen ratio in the fuel gas, and the flue-gas analysis, giving the total-nitrogen- (fuel nitrogen plus air nitrogen) carbon ratio in the flue gas, may be used (after the carbon gasified has been used to establish equivalent fuel-gas and flue-gas quantities) to calculate the quantity of air nitrogen in a specific quantity of flue gas. The equivalent quantity of air may then be determined, since the composition of air is known. It is reasonable to use an air composition of 79%m N_2 and 21%m O_2 for this purpose.

Now let us consider the secondary elements or compounds whose amount and distribution must be determined by calculation or analysis. Hydrogen is the most important of these. It may be present in air as water vapor. It is present in gaseous fuels in combination with carbon in relatively simple compounds. It is present in more complex compounds of carbon in liquid fuels. Solid fuels contain hydrogen in

adsorbed water and in extremely complex compounds of unknown structure. The latter compounds contain carbon, hydrogen, a small amount of oxygen, nitrogen, and sulfur. We commonly speak of three "kinds" of hydrogen in solid fuels. One is the hydrogen in adsorbed water. This water will simply be vaporized during combustion; it is not "made" nor "formed" by the combustion process. It is called *moisture* to emphasize the fact that it already exists as the compound H_2O in the fuel charged.

Another "kind" of hydrogen is that equivalent to the oxygen in the complex compounds in the fuel. It is called *combined* hydrogen and is treated as though it were already combined with oxygen in the proportions H_2O. This concept of "combined" hydrogen (said to be in "combined" water) is artificial. Except for the hydrogen in the moisture, none of the hydrogen in the coal is combined with oxygen in the ratio H_2O. The "combined-water" concept is used simply for convenience, for two reasons. The first reason is that it simplifies the calculations. The second reason is that its widespread adoption standardizes the calculation method and facilitates comparison of the calculations of different operators.

The third "kind" of hydrogen is called *net* hydrogen. It may be defined as that hydrogen which requires air oxygen for its combustion. Net hydrogen plus combined hydrogen are the total hydrogen of dry coal. The total hydrogen of wet coal includes moisture hydrogen.

A complete material balance requires determination of the fate of the hydrogen. An ash balance plus coal and refuse analyses can reveal the amounts of net and combined hydrogen in the refuse and the amount of water vapor in the flue gas derived from net and combined hydrogen in the coal. All the moisture in the coal and air is also in the flue gas. Therefore, if the flue gas, coal, and air have been "tied" together by carbon and nitrogen balances and if the moisture contents of coal and air are also known, the total water vapor in the flue gas can be determined by calculation. However, net-hydrogen determination on coal is difficult and is often omitted. In that event an alternative calculation procedure is employed. After the air has been tied in, the air oxygen supplied is known. If there are no other elements in the coal that can consume oxygen, the air oxygen has combined either with carbon or net hydrogen or has remained uncombined. Since the Orsat analysis of the flue gas reveals the oxygen which is combined with carbon and that which is uncombined, the amount combined with net hydrogen and thus the amount of net hydrogen burned can be determined by the difference between the air oxygen entering and the oxygen (in CO, CO_2, and as O_2) in the flue gas.

Another secondary element in the fuel is nitrogen. Appreciable quantities of the element may be present in gaseous fuels. This "fuel

nitrogen" is handled as described above in the nitrogen balance so that it will not be confused with air nitrogen and lead to erroneous calculations. The quantity of nitrogen in solid fuels is very small and may be neglected in the nitrogen balance.

The only other material of importance is the sulfur in solid fuels. It may be present as organic sulfur or as iron sulfide (FeS_2 iron pyrites). Organic sulfur is sulfur in the complicated carbon-hydrogen-oxygen complexes. This sulfur consumes air oxygen to form SO_2 or SO_3. Iron pyrites in the solid fuel complicates calculations in two ways. The sulfur consumes air oxygen, and the iron not only consumes air oxygen to form Fe_2O_3 (thus complicating the ash balance) but the Fe_2O_3 also may absorb some of the SO_3 formed. If appreciable amounts of sulfur are present, the details of calculation and analysis are much more tedious. The discussion of pyrites burners in a later section of this chapter reveals the methods of calculation that must be employed. In order to prevent such complications from obscuring the more important aspects of combustion calculations, we shall consider only those coals which contain negligible sulfur.

Following is a discussion of individual streams, their analyses, and the conclusions which may be derived from the analyses.

Fuels. *Gases.* Gaseous fuels may occur naturally or be products or by-products of industrial processes. The following table gives approximate compositions for some of them.

Table 6-1. Typical Industrial Fuel Gases*

Constituents	Producer gas	Water gas	Coal gas	Carburetted water gas	Natural gas	Refinery gas
CO	25.3	38.3	5.9	25.7	.....	1.2
H_2	13.2	52.8	53.2	32.6	.....	13.1
CH_4	0.4	0.4	29.6	8.6	82.8	23.3
C_2H_6	.....	.....	.....	7.2	16.3	21.7
Illuminants (unsaturated hydrocarbons)	.....	.....	2.7	13.1	0.8	39.6
CO_2	5.4	5.5	1.4	6.1	0.1	0.1
O_2	0.5	0.1	0.7	0.6	.....	1.0
N_2	55.2	2.9	6.5	6.1		
Net heating value, Btu/ft³	129	295	548	603	1145	1468

* From John H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., p. 1577, McGraw-Hill Book Company, Inc., New York, 1950.

The method of analysis involves collecting a dry sample over mercury and subjecting this sample to a series of operations designed to remove

individual gases. The volume is measured before and after each processing step, and the analysis is reported on a volumetric (or mole) basis. Nitrogen is determined by the difference between 100% and the sum of the percentages of all other constituents. Drying of the sample is usually necessary because certain of the reactants used to absorb specific gases will react with water. In the event that no such reactant need be used, a saturated sample is collected, as in the Orsat analysis discussed previously. In either event, the gas analysis is on a dry basis, and water-vapor content must be determined separately. Gaseous fuels bring two "types" of heat to the furnace. One is sensible heat (above an arbitrary datum), and the other is potential heat, part or all of which will be released during combustion. The heating value of gaseous fuels is expressed as Btu/standard cubic foot. "Standard conditions" in the gas industry are 1 atm and 60°F. Since chemical engineers also call 1 atm and 32°F "standard conditions," such expressions as "standard conditions," "standard pressure and temperature," and "normal pressure and temperature" should not be used in lieu of a statement of the temperature and pressure when there is any possibility of misinterpretation. The heating value of a gaseous fuel may be determined experimentally or calculated from heat-of-combustion data and the gas analysis. A careful statement of the basis of the heating value must be made. Usually the heating value per cubic foot at 1 atm and 60°F is the total heat evolved by combustion with dry air when the fuel and air are at 60°F before burning and all the flue gases are cooled to 60°F after burning, with the water vapor condensed to liquid at that temperature. This quantity is called the *higher heating value* (HHV) or *gross heating value* (GHV). If the latent heat of the liquid water is subtracted from the higher heating value, the *lower heating value* (LHV) or *net heating value* is obtained. It is the heat that would have been generated if the flue gases had been cooled to 60°F, with the water remaining as vapor. When a heating value is given in a problem statement, it may be assumed to be the HHV unless otherwise noted, because it is this value which is usually reported.

Liquids. The commonest liquid fuels are light or heavy oils which are products or by-products of petroleum refining. They contain compounds of known structure but of higher molecular weight than the compounds of gaseous fuels. The analysis commonly made for use in combustion calculations gives the percentage by weight of each element. Liquid fuels contain carbon and hydrogen and negligible amounts of oxygen and ash. Their heating values are expressed in Btu/lb.

Solids. Solid fuels are coals and pre-coals. They presumably were formed from ancient vegetation. They contain elemental carbon, complex organic compounds of unknown structure, and mineral matter. The organic compounds contain carbon, hydrogen, oxygen, sulfur, and nitro-

gen. The mineral matter is noncombustible and forms the ash. Two types of analysis, called *proximate* and *ultimate*, are made on coal. The ultimate analysis reports the percentage by weight of ash and of each element in the coal. It may be made on dry or wet coal. The proximate analysis is obtained by an empirical procedure developed and standardized by the coal industry. It reports the percentage by weight of moisture, volatile combustible matter, fixed carbon, and ash. Both of these analyses are important from the standpoint of "classification" of coal in grades such as "anthracite," "semibituminous," and "bituminous." We shall not make this our concern in this text but shall consider the analyses of a particular coal in relation to each other and to the furnace calculation.

PROXIMATE ANALYSIS. Moisture content is determined by measuring the loss in weight of a sample heated for 1 hr at 104° to 110°C. The dried sample is then heated in a covered crucible for 7 min at 950°C and reweighed. The material lost is called *volatile combustible matter* (VCM). The VCM contains substantially all the hydrogen, oxygen (exclusive of that in moisture), sulfur, and nitrogen and a large amount of carbon. The remaining combustible is considered to be pure carbon. It is called *fixed carbon* (FC), and its percentage is calculated, after the ash has been measured by complete combustion of the sample in air at 725°C, by subtracting the sum of the percentages of moisture, VCM, and ash from 100. It is convenient for calculation purposes to consider the oxygen in the VCM to be combined with an equivalent amount of hydrogen. The remaining hydrogen is called "net" hydrogen. It requires air oxygen for its combustion. In keeping with this approach, we say that the VCM consists of combined water and volatile hydrocarbons which contain small amounts of nitrogen and sulfur in their structures.

ULTIMATE ANALYSIS. The technique of the ultimate analysis need not concern us except that we should note that the oxygen is determined by difference. Therefore all errors accumulate in the "%w oxygen" figure and subsequently alter the values of combined and "net" hydrogen.

The carbon reported in the ultimate analysis is the sum of that present in the VCM and FC. The hydrogen is in the VCM (net and combined) and in moisture (if the coal is wet). Oxygen is in the VCM (combined) and in moisture. Nitrogen is in the VCM, and sulfur is in the VCM (organic) or in mineral sulfides (usually FeS_2). In the coals that we shall consider, nitrogen and sulfur may be neglected except in the statement of the analysis, where their omission would cause serious error in the oxygen value reported.

The relation between the ultimate and proximate analyses is illustrated in the following example.

Example 6-1. Complete the following coal analyses. The analyses were all made on the same coal, which had been "air-dried."

Ultimate		Proximate		Modified ultimate
C	78%w	FC	65%w	C
H*	6	Moisture	4	Moisture
O*		VCM		Combined H_2O
N*	3	Ash		Net H
S	2	.....		N + S
Ash	4	.....		Ash

* In accord with common practice we use the symbols H,O,N, rather than H_2,O_2,N_2, when giving a coal analysis. This was done originally to emphasize the fact that the analysis is on a weight basis. However, in our opinion it is reasonable to use the symbol for the common molecular form of an element when stating a weight (as in 5 lb H_2) and we shall do so in the calculations.

Solution. The only quantity missing in the ultimate analysis is oxygen. It may be calculated, by difference, to be 7%w.

Since the analyses were all on the same basis ("air-dried" coal), each should show 4%w ash, as measured in the ultimate analysis.

The VCM may next be calculated by difference to be 27%w (100 − 65 − 4 − 4). This completes the proximate analysis.

The modified ultimate analysis remains to be completed. Carbon content is 78%w, moisture is 4%w, N + S is 5%w, and ash is 4%w. Since net hydrogen is the hydrogen requiring air oxygen for combustion, it may be determined by subtracting the hydrogen equivalent to 7 lb of oxygen from the total hydrogen.

$$(7 \text{ lb } O_2)\left(\frac{2 \text{ lb } H_2}{16 \text{ lb } O_2}\right) = 0.88 \text{ lb } H_2 \text{ in moisture and combined } H_2O$$

$$6 \text{ lb total } H_2 - 0.88 \text{ lb } H_2 = 5.12 \text{ lb net } H_2$$

Combined H_2O may now be calculated by difference to be

$$3.88\%w\ (100 - 78 - 4 - 5.12 - 5 - 4)$$

Ultimate		Proximate		Modified ultimate	
C	78%w	FC	65%w	C	78
H	6	Moisture	4	Moisture	4
O	7	VCM	27	Combined H_2O	3.88
N	3	Ash	4	Net H	5.12
S	2	.....		N + S	5
Ash	4	.....		Ash	4

Example 6-2. Calculate the ultimate analysis of the VCM from the following analyses of a coal. Both analyses are on "air-dried" coal.

Ultimate		*Proximate*	
C	79.9	Moisture	3.2
H	4.85	FC	69.3
O	6.76	VCM	21.0
S	0.69	Ash	6.5
N	1.30		
Ash	6.50		

Solution

Basis: 100 lb coal as analyzed; 21 lb of VCM is present. From the proximate analysis it may be seen that the moisture, fixed carbon, and ash are not VCM. Therefore, if we subtract these materials from the quantities in the ultimate analysis, we shall have left the components comprising the 21 lb of VCM.

		%w
C: 79.9 − 69.3	= 10.60	50.5
H: 4.85 − (3.2 lb moisture) $\left(\frac{2 \text{ lb } H_2}{18 \text{ lb moisture}}\right)$	= 4.49	21.4
O: 6.76 − (3.2)($^{16}/_{18}$)	= 3.92	18.65
S:	= 0.69	3.28
N:	= 1.30	6.19
	21.00	100.02

The heating value of a solid fuel is expressed in Btu/lb. The terms "gross" or "higher" and "net" or "lower" have the significance explained previously for gaseous fuels.

REFUSE. A furnace normally fails to gasify some of the combustible matter if a solid fuel is fired.

The solid material discharged to waste is called *refuse*, not ash. The term "ash" is reserved for noncombustible matter only. A standard industrial furnace carries the fuel on an "endless" chain grate. Experience has shown that the refuse is a mixture of ash, "coked" coal (moisture and VCM driven off; only FC and ash remain), and dry "uncoked" (or "green") coal (moisture driven off; the VCM, FC, and ash remain). The loss of VCM occurs quickly and over a very narrow temperature range, and rarely does coal with only part of its VCM volatilized fall into the refuse. When this does occur, an ultimate analysis of the refuse must be made for use in calculations. In this book we shall consider only the common case, where combustible loss is due to coked and uncoked coal.

Example 6-3. A furnace is fired with coal containing 6% moisture, 18% VCM, 67% FC, and 9% ash. The refuse analysis shows 5% VCM,

23% FC, and 62% ash. The higher heating value of the coal "as fired" is 14,300 Btu/lb. Calculate the percentage of the heating value of the coal that is lost in the refuse. The moisture in the refuse is due to "wetting down" to prevent dusting. It is not moisture from the original coal.

Solution 1. The ash is the key component tying the refuse stream to the feed. Pick a basis of a definite weight of coal and calculate the relative quantity of refuse by an ash balance. Calculate the amounts of VCM and FC lost in the refuse from the refuse quantity and refuse analysis.

Calculate the higher heating value of the VCM as follows: Pick a basis of 1 lb of coal and subtract the heating value of the FC in it [(lb FC) (Btu/lb C)] from the HHV. The quantity obtained is the heat generated by the VCM. Divide this heat quantity by the pounds of VCM in the pound of coal to obtain the higher heating value of VCM in Btu/lb of VCM.

Returning to the original basis, multiply the amounts of FC and VCM in the refuse by their respective heating values and add the heat quantities. The sum, divided by the heating value of the amount of coal chosen as a basis, multiplied by 100, is the percentage of the heating value of the coal lost in the refuse.

Basis: 100 lb of coal as fired

$$(9 \text{ lb ash}) \left(\frac{100 \text{ lb refuse}}{62 \text{ lb ash}}\right) = 14.51 \text{ lb refuse}$$

$$(14.51 \text{ lb refuse}) \left(\frac{0.05 \text{ lb VCM}}{\text{lb refuse}}\right) = 0.725 \text{ lb VCM}$$

$$(14.51 \text{ lb refuse}) \left(\frac{0.23 \text{ lb FC}}{\text{lb refuse}}\right) = 3.34 \text{ lb FC}$$

To find HV of VCM:

Basis: 1 lb of coal as fired

$$(0.67 \text{ lb FC}) \left(\frac{14{,}550 \text{ Btu}}{\text{lb C}}\right) = 9750 \text{ Btu generated by FC}$$

$$14{,}300 - 9750 = 4550 \text{ Btu} = \text{HHV of } 0.18 \text{ lb VCM}$$

$$\frac{4550 \text{ Btu}}{0.18 \text{ lb VCM}} = \frac{25{,}300 \text{ Btu}}{\text{lb VCM}}$$

Basis: 100 lb of coal as fired

$$(0.725 \text{ lb VCM in refuse}) \left(\frac{25{,}300 \text{ Btu}}{\text{lb VCM}}\right) = 18{,}320 \text{ Btu lost due to VCM loss}$$

$$(3.34 \text{ lb FC}) \left(\frac{14{,}550 \text{ Btu}}{\text{lb FC}}\right) = 48{,}600 \text{ Btu lost due to FC loss}$$

$$\left(\frac{48{,}600 + 18{,}320}{(14{,}300)(100)}\right)(100) = 4.68\% \text{ of heating value lost in refuse}$$

Note that the solution is valid only if the nature of the VCM in the refuse is the same as it is in the coal and that this is true only if no partially coked coal falls through the grate.

Solution 2. After calculating the quantity of VCM and FC lost relative to a certain amount of coal charged, proceed as follows:

Calculate the amount of original coal that would contain all the VCM in the refuse and label this quantity "green coal" or "uncoked coal." From the original coal analysis, calculate the amount of FC in this uncoked coal. Subtract the FC in the uncoked coal from the total FC in the refuse and label the result "FC in coked coal in refuse." Multiply the amount of green coal by the heating value of green coal and the amount of coked-coal FC by the heating value of carbon (14,550 Btu/lb). The sum of the two heat quantities is the total heat loss and may be expressed as a percentage of the total heating value of the amount of coal charged.

Basis: 100 lb of coal as fired

0.725 lb VCM and 3.34 lb FC are in the refuse

$$(0.725 \text{ lb VCM}) \left(\frac{100 \text{ lb green coal}}{18 \text{ lb VCM}}\right) = 4.03 \text{ lb green coal}$$

$$(4.03 \text{ lb green coal}) \left(\frac{67 \text{ lb FC}}{100 \text{ lb green coal}}\right) = 2.70 \text{ lb FC in green coal}$$

$$3.34 - 2.70 = 0.64 \text{ lb FC in coked coal}$$

$$(4.03 \text{ lb green coal}) \left(\frac{14{,}300 \text{ Btu}}{\text{lb coal}}\right) = 57{,}600 \text{ Btu loss due to green-coal loss}$$

$$(0.64 \text{ lb FC in coked coal}) \left(\frac{14{,}550 \text{ Btu}}{\text{lb coal}}\right) = 9330 \text{ Btu loss due to coked-coal loss}$$

$$\left(\frac{57{,}600 + 9330}{(14{,}300)(100)}\right)(100) = 4.68\% \text{ of heating value lost in refuse}$$

Note that each method makes the assumption that VCM in refuse is identical in nature with VCM in coal. This can be true only if all the VCM in the refuse is in uncoked coal. As mentioned previously, an ultimate analysis of the coal and refuse would be required if an appreciable amount of partially coked coal were in the refuse. Note also that the HHV is given for the coal. This is the heating value that is determined experimentally; it is therefore the one normally reported by the laboratory. In the improbable event that only the LHV is known, the calculations must be modified if the percentage of the LHV lost in refuse is to be calculated. Such a calculation is so seldom made that it is not worthwhile to include the details of it here.

Flue Gases. Flue, or stack, gases contain CO_2, CO, O_2, N_2, and water vapor. The oxides of carbon are formed from the fuel's carbon. All the

carbon that burns (either to CO or to CO_2) is in the flue gas. The free oxygen is air oxygen that has remained uncombined. The nitrogen comes from air and from the fuel (from certain gaseous fuels). The water vapor is moisture from air and fuel (solid fuels), combined water from solid fuels, and water formed by the combustion of net hydrogen. An ideal furnace would burn all the combustibles charged (losing none in refuse) and would burn them completely (net H_2 to H_2O, all C to CO_2) and would require only that amount of air equivalent to the oxygen required to burn net hydrogen and to burn carbon to CO_2. A real furnace may burn all the fuel charged (it usually does if the fuel is a liquid or a gas), but it almost invariably fails to achieve complete combustion of the fuel burned. In an effort to push the combustion toward completion, extra air is supplied. It is common practice to relate the air supplied to the air requirement of an ideal furnace by calculating the "per cent excess air" based on the air requirement of an ideal furnace. The "per cent excess oxygen" is the same as the per cent excess air. A typical calculation is illustrated below.

Example 6-4. A fuel gas containing 80%m CH_4 and 20%m C_2H_6 is burned with dry air. Sixty per cent of the carbon burned goes to CO_2, the rest going to CO. Fifty per cent excess air is used. Calculate the number of moles of each constituent of the wet flue gas produced by combustion of 100 mole of fuel gas, and also the Orsat analysis of the flue gas.

Method. Pick a basis of 100 mole of fuel gas and list the number of moles of carbon and hydrogen present. Calculate the quantity of oxygen necessary to burn all the fuel completely. This is the oxygen required. Since 50% of the amount of oxygen required is the amount of excess oxygen, 1.5 times the oxygen required is the oxygen supplied. Multiply the oxygen supplied by the moles of nitrogen per mole of oxygen (in air) to obtain the nitrogen supplied. All the nitrogen supplied will be in the flue gas as molecular nitrogen. All the carbon in the fuel charged (also called "fuel fired") to the furnace will be in the flue gas since all the fuel is burned. Sixty per cent of the carbon will be CO_2; 40% will be CO. All the hydrogen will be in the flue gas as water vapor. Calculate the amount of oxygen actually consumed to burn the carbon and hydrogen. Subtract the oxygen consumed from the oxygen supplied to obtain the oxygen unconsumed. The CO_2, CO, H_2O, unconsumed O_2, and N_2 are the constituents of the flue gas.

Solution

Basis: 100 mole of fuel gas. Equations:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$$
$$C + O_2 \rightarrow CO_2$$
$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

Compound	lbmole	lbatom C	lbmole H_2	lbmole O_2 required
CH_4.....	80	80	160	160
C_2H_6.....	20	40	60	70
	100	120	220	230

$$(230 \text{ mole } O_2 \text{ required})(1.5) = 345 \text{ mole } O_2 \text{ supplied}$$

$$(345 \text{ mole } O_2)\left(\frac{79 \text{ mole } N_2}{21 \text{ mole } O_2}\right) = 1300 \text{ mole } N_2 \text{ supplied}$$

$$(120 \text{ mole C burned})\left(\frac{0.6 \text{ mole } CO_2 \text{ formed}}{\text{mole C burned}}\right) = 72 \text{ mole } CO_2 \text{ formed}$$

$$120 \text{ mole C burned} - 72 \text{ mole C to } CO_2 = 48 \text{ mole CO formed}$$

$$345 \text{ mole } O_2 \text{ supplied} - 72 \text{ mole } O_2 \text{ to } CO_2 - 24 \text{ mole } O_2 \text{ to CO} - 110 \text{ mole } O_2 \text{ to } H_2O = 139 \text{ mole } O_2 \text{ unconsumed}$$

Flue-gas Constituents per 100 Mole of Fuel Gas

Compound	Mole	Mole C	Mole H_2	Mole O_2	Orsat analysis
CO_2.....	72	72	...	72	4.62
CO.....	48	48	...	24	3.08
O_2.....	139	...	...	139	8.91
N_2.....	1300	...	...	...	83.39
H_2O.....	220	...	220	110	
	1779	120	220	345	100.00
	− 220				
	1559 mole dry flue gas				

Note that the flue-gas analysis, as explained previously, does not include the water vapor. Note also that the per cent excess air is based on the requirements of an ideal furnace and therefore depends only on the relative amounts of fuel charged and air supplied. As long as the ratio of air to fuel is constant, the per cent excess air is constant whether or not the furnace is burning the fuel well (high percentage of fuel burned; high CO_2 formation) or poorly (refuse losses; high CO formation). Therefore a comparison of furnaces on the basis of excess air is not a good comparison of efficiency. The real comparison of efficiency is made by calculating the percentage of fuel heating value that is not utilized. Loss of heating value due to unburned combustible in refuse has been discussed. Heat loss in flue gas will be discussed at the end of this section.

Deductions from Orsat Analysis. If the fuel burned contains no nitrogen, three major deductions may be made from the flue-gas analysis

alone. The first concerns the amount of air supplied per mole of flue gas. All the air nitrogen appears in the gas analysis. Nitrogen therefore is the key component relating air and flue gas. The second deduction concerns the amount of hydrogen burned per mole of flue gas. Since water vapor does not "appear" in the Orsat analysis, the air oxygen that reacts with hydrogen "disappears." Therefore calculation of air oxygen supplied (from nitrogen content) and oxygen present (in CO_2, CO, and O_2) permits determination of oxygen disappearance and of hydrogen burned. The third deduction concerns the amount of carbon burned per mole of dry flue gas, which may be determined directly from the gas analysis. Carbon burned is the key component tying the fuel and flue gas together.

Example 6-5. The analysis of a flue gas from a fuel gas containing no nitrogen is 4.62% CO_2, 3.08% CO, 8.91% O_2, and 83.39% N_2. Calculate the following:

a. Moles of dry air supplied per mole of dry flue gas
b. Per cent excess air if all the fuel is burned
c. The amount of net hydrogen burned per mole of dry flue gas
d. Pounds of fuel burned per mole of dry flue gas
e. The analysis of the fuel gas, which is a mixture of CH_4 and C_2H_6

Method. Pick a basis of 100 mole of dry flue gas. Calculate the air equivalent to the nitrogen. Calculate part *a*. Add the oxygen in CO_2, CO, and O_2. The sum is the oxygen appearing in the flue gas. Subtract the oxygen appearing from the oxygen supplied to obtain the oxygen that burned net hydrogen. Calculate part *c*. Calculate the oxygen required for ideal combustion of the carbon and add to the oxygen burning net hydrogen. The sum is the oxygen requirement of an ideal furnace. Subtract it from the oxygen supplied to obtain excess oxygen. Calculate part *b*. Calculate the pounds of carbon and hydrogen burned. Calculate part *d*. Write a carbon balance and a hydrogen balance for the fuel gas and calculate part *e*.

Solution

Basis: 100 mole of dry flue gas

Compound	Mole	Mole C	Mole O_2
CO_2	4.62	4.62	4.62
CO	3.08	3.08	1.54
O_2	8.91	....	8.91
N_2	83.39		
	100.00	7.70	15.07

$$(83.39 \text{ mole } N_2)\left(\frac{100 \text{ mole dry air}}{79 \text{ mole } N_2}\right) = 105.5 \text{ mole air supplied}$$

a. 1.055 mole air supplied per mole dry flue gas

$$105.5 - 83.39 = 22.11 \text{ mole } O_2 \text{ supplied}$$
$$22.11 - 15.07 \text{ mole } O_2 \text{ appearing} = 7.04 \text{ mole } O_2 \text{ disappearing}$$
$$(2)(7.04) = 14.08 \text{ mole net } H_2 \text{ burned}$$

c. 0.1408 mole net H_2 burned per mole of dry flue gas

$$7.70 \text{ mole } O_2 \text{ required for C} + 7.04 \text{ mole } O_2 \text{ required for } H_2 = 14.74 \text{ mole } O_2 \text{ required for ideal furnace}$$
$$22.11 \text{ mole } O_2 \text{ supplied} - 14.74 \text{ mole } O_2 \text{ required} = 7.37 \text{ mole } O_2 \text{ excess}$$

b. $$\left(\frac{7.37 \text{ mole } O_2 \text{ excess}}{14.74 \text{ mole } O_2 \text{ required}}\right)(100) = 50\% \text{ excess air}$$

$$(7.70 \text{ mole C burned})\left(\frac{12 \text{ lb C}}{\text{mole C}}\right) = 92.4 \text{ lb C burned}$$
$$(14.08 \text{ mole } H_2 \text{ burned})\left(\frac{2 \text{ lb } H_2}{\text{mole } H_2}\right) = 28.16 \text{ lb H burned}$$
$$92.4 + 28.2 = 120.6 \text{ lb fuel burned}$$

d. 1.206 lb fuel burned per mole dry flue gas

e. Let X = mole of CH_4 in fuel gas

Y = mole of C_2H_6 in fuel gas

Then,
$$X + 2Y = 7.70 \text{ mole C in fuel gas}$$
$$2X + 3Y = 14.08 \text{ mole } H_2 \text{ in fuel gas}$$
$$X = 5.06 \quad 79.3\%\text{m } CH_4$$
$$Y = 1.32 \quad 20.7\%\text{m } C_2H_6$$
$$\text{Total} = 6.38$$

Compare the last two illustrations.

Certain fuel gases contain appreciable nitrogen. In order to make deductions from the flue-gas analysis when such a fuel is burned, it is necessary to know the nitrogen-carbon ratio in the fuel. A fuel-gas analysis will give this figure. Then the fuel nitrogen in a particular quantity of flue gas may be calculated and subtracted from the total nitrogen to obtain air nitrogen.

Heat Losses in Flue Gases. In making a heat balance around a furnace, the same datum plane must be taken for each stream. Since the heating value of the coal is based on a datum of 60°F, H_2O in the liquid state, this is the datum normally chosen for all streams. The refuse heat loss should include sensible heat of all refuse above 60°F as well as loss of potential heat due to loss of combustibles, but the sensible-heat loss may be neglected because the total weight of material in the refuse is relatively small. Heat losses in the flue gas are of three "kinds." Sensible heat is lost because the gas leaves at an elevated temperature; potential heat of combustion is lost because the gas contains carbon

monoxide; and latent heat is lost because the gas contains water vapor. An adequate method for computing the total heat loss due to the flue gas is outlined below.

Example 6-6. The flue gas of Example 6-5 leaves at 700°F and 1 atm. The air supplied to the furnace was dry. Calculate the amount of heat lost per 100 mole of dry flue gas.

Solution

Heat loss = heat of combustion of CO + sensible heat loss in all gases + latent heat loss in water vapor

Basis: 100 mole of dry flue gas. Datum 60°F, H_2O liquid.

$$(3.08 \text{ mole CO})\left(\frac{68{,}000 \text{ cal}}{\text{gmole}}\right)\left(\frac{1.8 \text{ Btu/lbmole}}{\text{cal/gmole}}\right)$$

= 377,000 Btu loss due to CO

The latent heat of vaporization of water at 60°F = 1060 Btu/lb.

$$(14.08 \text{ mole water vapor})\left(\frac{18 \text{ lb } H_2O}{\text{mole } H_2O}\right)\left(\frac{1060 \text{ Btu}}{\text{lb } H_2O}\right)$$

= 268,000 Btu loss due to latent heat in H_2O

Sensible-heat Losses above 60°F

Gas	Mole	Mean C_p between 0°F and 700°F, Btu/(mole)(F°)	Btu/F° $\frac{\text{Btu}}{(\text{mole})(\text{F°})}$(mole)
CO_2.....	4.62	10.15	46.8
CO.....	3.08	7.12	21.9
O_2.....	8.91	7.32	65.2
N_2.....	83.39	7.09	591
H_2O.....	14.08	8.30	116.8
	114.08		841.7

$$\text{Total sensible heat loss} = \frac{841.7 \text{ Btu}}{\text{F°}}(700 - 60)\text{ F°} = 538{,}000 \text{ Btu}$$

$$\text{Heat loss} = 377{,}000 + 538{,}000 + 268{,}000 = \frac{1{,}183{,}000 \text{ Btu}}{100 \text{ mole dry flue gas}}$$

Note that the total heat content of the water vapor above liquid water at 60°F was calculated by adding the latent heat of vaporization at 60°F to the sensible heat necessary to heat the vapor from 60°F to 700°F. This method gives the heat content of water vapor at 700°F and at a pressure corresponding to the vapor pressure of water at 60°F. The partial pressure of the water vapor in flue gases is sufficiently close to this pressure that no significant error is introduced by the method. To check this, calculate the partial pressure of the water vapor in the flue

gas in Example 6-6, and from Appendix E determine the saturation temperature and latent heat of vaporization at this pressure. Then calculate the heat required to bring liquid water from 60°F to the saturation temperature (corresponding to the actual partial pressure of the water vapor), the heat required to vaporize the water at the saturation temperature, and the heat required to raise the vapor to the flue-gas temperature. The sum of these heat quantities is equal (within slide-rule accuracy) to the total heat content of the water vapor calculated in the example.

Comprehensive Problems. The following problems illustrate the application of the methods thus far discussed to the solution of comprehensive furnace problems.

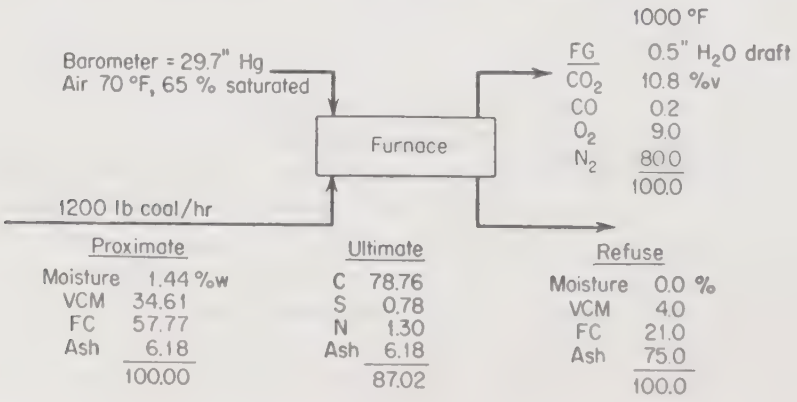
Example 6-7. Coal is charged to a furnace at the rate of 1200 lb/hr. Analysis of the coal and flue gas shows the following:

Proximate		Ultimate (in part)		Stack gas	
Moisture	1.44%w	C	78.76%w	CO_2	10.8%v
VCM	34.61%w	S	0.78%w	CO	0.2%v
FC	57.77%w	N	1.30%w	O_2	9.0%v
Ash	6.18%w	Ash	6.18%w	N_2	80.0%v
					100.00

The dry refuse contains 4%w VCM, 21%w FC, 75%w ash. Air supplied is at 70°F, 65% saturated. The vapor pressure of water at 70°F is 0.41 psia. Barometer = 29.7 in. Hg. Pressure at the entrance to the stack is 0.5 in. H_2O. Calculate the following:

a. Complete ultimate analysis of the coal
b. Per cent excess air
c. Cubic feet of air per minute
d. Cubic feet of flue gas at 1000°F to stack per minute

Method. First draw a diagram and note all data.



Pick a basis of 100 lb of coal. Calculate the equivalent quantity of refuse by an ash balance. Calculate the %w C in the VCM from the data of the proximate and ultimate analyses. Calculate the carbon lost in the refuse and then the moles of carbon burned. The carbon burned is the key component relating the coal and flue gas. Compute the amount (poundmoles) of dry flue gas from the carbon burned and the gas analysis. From oxygen disappearance, calculate the amount of net hydrogen burned. The percentage of total net hydrogen lost in the refuse is equal to the percentage of VCM lost. Calculate this quantity from the amounts of VCM in the fuel and refuse, and then compute the total net hydrogen in the fuel. The items missing in the ultimate analysis are hydrogen and oxygen. Their combined weight may be determined by difference. It is the weight of net hydrogen, combined water, and moisture. Since the amount of net hydrogen is now known, the total water may be determined, and then the ultimate analysis may be expressed as %w of C, H, N, O, S, and ash. (Answer to *a*.)

Calculate "oxygen required" from the ultimate analysis. By a nitrogen balance, determine the moles of oxygen and dry air supplied. Calculate the per cent excess air. (Answer to *b*.) Compute the volume of the dry air supplied at 70°F and the partial pressure of dry air. This is the volume of wet air supplied at 70°F and barometric pressure, per 100 lb of coal. Calculate the cubic feet of wet air per minute. (Answer to *c*.)

The number of moles of dry flue gas is known. The water in it because of combustion of net hydrogen is known. Calculate the moles of water entering with air. Calculate the moles of combined water volatilized. (Remember that % VCM lost = % combined H_2O lost.) Add the moles of "moisture" to the items above to find the total moles of wet flue gas, and compute its volume at 1000°F and 0.5 in. H_2O draft. (Answer to *d*.)

Solution

Basis: 100 lb of coal as fired

Amount of refuse:

$$(6.18 \text{ lb ash}) \left(\frac{100 \text{ lb refuse}}{75 \text{ lb ash}} \right) = 8.25 \text{ lb refuse}$$

%w C in VCM:

$$78.76 \text{ lb C in coal} - 57.77 \text{ lb FC in coal} = 20.99 \text{ lb C in VCM}$$

$$\left(\frac{20.99 \text{ lb C in VCM in coal}}{34.61 \text{ lb VCM in coal}} \right) (100) = 60.6\% \text{w C in VCM}$$

Mole C burned:

$$(8.25 \text{ lb refuse})\left(\frac{4 \text{ lb VCM}}{100 \text{ lb refuse}}\right)\left(\frac{60.6 \text{ lb C}}{100 \text{ lb VCM}}\right)$$
$$= 0.20 \text{ lb C in VCM in refuse}$$

$$(8.25 \text{ lb refuse})\left(\frac{21 \text{ lb FC}}{100 \text{ lb refuse}}\right) = 1.73 \text{ lb FC in refuse}$$

$$1.73 + 0.20 = 1.93 \text{ lb C lost in refuse}$$

$$78.76 \text{ lb C fired} - 1.93 \text{ lb C lost} = 76.83 \text{ lb C burned}$$

$$(76.83 \text{ lb C})\left(\frac{1 \text{ mole C}}{12 \text{ lb C}}\right) = 6.38 \text{ mole C burned}$$

Mole DFG (dry flue gas):

$$(6.38 \text{ mole C burned})\left(\frac{100 \text{ mole DFG}}{(10.8 + 0.2) \text{ mole C}}\right) = 58.1 \text{ mole DFG}$$

Mole net H_2 burned:

Compound	%v	Mole	Mole C	Mole O_2
CO_2	10.8	6.26	6.26	6.26
CO	0.2	0.12	0.12	0.06
O_2	9.0	5.23		5.23
N_2	80.0	46.49		
		58.10	6.38 ← (check)	11.55

$$(46.49 \text{ mole } N_2)\left(\frac{21 \text{ mole } O_2}{79 \text{ mole } N_2}\right) = 12.35 \text{ mole } O_2 \text{ supplied}$$

$$12.35 - 11.55 = 0.80 \text{ mole } O_2 \text{ disappear}$$
$$\approx 1.6 \text{ mole net } H_2 \text{ burned}$$

Pounds net H_2 in fuel:

$$(8.25 \text{ lb refuse})\left(\frac{4 \text{ lb VCM}}{100 \text{ lb refuse}}\right) = 0.33 \text{ lb VCM in refuse}$$

$$\left(\frac{0.33 \text{ lb VCM in refuse}}{34.61 \text{ lb VCM in coal fired}}\right)(100) = 0.953\% \text{ of VCM lost}$$
$$= \% \text{ of net } H_2 \text{ lost} = \% \text{ of combined } H_2O \text{ lost}$$

$$100 - 0.953 = 99.048\% \text{ of net } H_2 \text{ burned}$$

$$(1.6 \text{ mole net } H_2 \text{ burned})\left(\frac{2 \text{ lb } H_2}{\text{mole } H_2}\right)\left(\frac{1 \text{ lb net } H_2 \text{ in coal}}{0.9905 \text{ lb net } H_2 \text{ burned}}\right)$$
$$= 3.23 \text{ lb net } H_2 \text{ in coal}$$

a. Complete ultimate analysis of the coal

lb H_2 + lb O_2 in coal = 100 − (78.76 lb C + 0.78 lb S + 1.30 lb N_2 + 6.18 lb ash) = 12.98 lb (net H_2 + moisture + combined H_2O)

12.98 lb − 3.23 = 9.75 lb total H_2O

$$(9.75 \text{ lb } H_2O)\left(\frac{2 \text{ lb } H_2}{18 \text{ lb } H_2O}\right) = 1.08 \text{ lb } H_2 \text{ in moisture and combined } H_2O$$

9.75 − 1.08 = 8.67 lb O_2 in moisture and combined H_2O

1.08 + 3.23 = 4.31 lb total H_2

The ultimate analysis is

78.76%w C, 4.31%w H, 8.67%w O, 1.30% N, 0.78% S, 6.18% ash

Oxygen required for ideal combustion (sometimes called "theoretical oxygen"):

$$(78.76 \text{ lb C})\left(\frac{1 \text{ mole C}}{12 \text{ lb C}}\right)\left(\frac{1 \text{ mole } O_2}{1 \text{ mole C}}\right) = 6.56 \text{ mole } O_2 \text{ required by C}$$

$$(3.23 \text{ lb net } H_2)\left(\frac{1 \text{ mole } H_2}{2 \text{ lb } H_2}\right)\left(\frac{1 \text{ mole } O_2}{2 \text{ mole } H_2}\right) = 0.808 \text{ mole } O_2 \text{ required by net } H_2$$

6.56 + 0.81 = 7.37 mole O_2 required

b. Per cent excess air

$$(46.49 \text{ mole } N_2)\left(\frac{21 \text{ mole } O_2 \text{ supplied}}{79 \text{ mole } N_2}\right) = 12.35 \text{ mole } O_2 \text{ supplied}$$

12.35 − 7.37 = 4.98 mole excess O_2

$$\left(\frac{4.98 \text{ mole excess } O_2}{7.37 \text{ mole } O_2 \text{ required}}\right)(100) = 67.6\% \text{ excess air}$$

c. Cubic feet of air per minute

46.49 mole N_2 + 12.35 mole O_2 = 58.84 mole dry air supplied

Partial pressure of water vapor

= (vapor pressure of water) (% saturation)

Partial pressure H_2O = (0.65)(0.41 psia) = 0.2665 psia

$$(0.2665 \text{ psia})\left(\frac{29.9 \text{ in. Hg}}{14.7 \text{ psi}}\right) = 0.542 \text{ in. Hg}$$

29.7 in. Hg total pressure − 0.542 in. Hg partial pressure H_2O = 29.2 in. Hg partial pressure of dry air

$$\left[(58.84 \text{ mole dry air})\left(\frac{359 \text{ ft}^3}{\text{mole}}\right)\right]\left(\frac{29.9 \text{ in. Hg}}{29.2 \text{ in. Hg}}\right)\left(\frac{530°\text{R}}{492°\text{R}}\right) = 23{,}300 \text{ ft}^3$$

23,300 ft³ of dry air at 70°F and 29.2 in. Hg:

23,300 ft³ of wet air at 70°F and 29.7 in. Hg per 100 lb coal:

$$\left(\frac{23{,}300 \text{ ft}^3 \text{ of wet air}}{100 \text{ lb coal}}\right)\left(\frac{1200 \text{ lb coal}}{\text{hr}}\right)\left(\frac{\text{hr}}{60 \text{ min}}\right) = 4660 \text{ ft}^3 \text{ wet air supplied/min}$$

d. Cubic feet flue gas per minute

$$\text{Mole DFG} = 58.1 \text{ mole}$$

$$\text{Mole } H_2O \text{ from net } H_2 \text{ combustion} = 1.6 \text{ mole}$$

$$\text{Mole } H_2O \text{ from moisture in coal} = (1.44 \text{ lb } H_2O)\left(\frac{1 \text{ mole } H_2O}{18 \text{ lb } H_2O}\right) = 0.08 \text{ mole}$$

Mole H_2O from combined H_2O:

$$9.75 \text{ lb total } H_2O - 1.44 \text{ lb moisture} = 8.31 \text{ lb combined } H_2O$$

$$(8.31 \text{ lb combined } H_2O \text{ charged})\left(\frac{0.9905 \text{ lb combined } H_2O \text{ vaporized}}{\text{lb combined } H_2O \text{ charged}}\right) = 8.23 \text{ lb combined } H_2O \text{ vaporized}$$

$$(8.23 \text{ lb combined } H_2O)\left(\frac{1 \text{ mole } H_2O}{18 \text{ lb } H_2O}\right) = 0.457 \text{ mole combined } H_2O \text{ in flue gas}$$

Mole H_2O from air:

$$(58.84 \text{ mole dry air})\left(\frac{0.542 \text{ mole } H_2O}{29.2 \text{ mole dry air}}\right) = 1.09 \text{ mole } H_2O \text{ from air}$$

$$58.1 \text{ mole DFG} + 1.6 \text{ mole } H_2O \text{ from net } H_2 + 0.08 \text{ mole moisture} + 0.457 \text{ mole combined } H_2O + 1.09 \text{ mole } H_2O \text{ from air} = 61.33 \text{ mole WFG}$$

$$\left(\frac{61.33 \text{ mole WFG}}{100 \text{ lb coal}}\right)\left(\frac{1200 \text{ lb coal}}{\text{hr}}\right)\left(\frac{\text{hr}}{60 \text{ min}}\right) = \frac{12.25 \text{ mole WFG}}{\text{min}}$$

$$(0.5 \text{ in. } H_2O)\left(\frac{1 \text{ in. Hg}}{13.6 \text{ in. } H_2O}\right) = 0.037 \text{ in. Hg draft} \approx 0.04 \text{ in. Hg}$$

Pressure at entrance to stack $= 29.7 - 0.04 = 29.66$ in. Hg absolute

$$\left[\left(\frac{12.25 \text{ mole flue gas}}{\text{min}}\right)\left(\frac{359 \text{ ft}^3}{\text{mole}}\right)\right]\left(\frac{29.9 \text{ in. Hg}}{29.66 \text{ in. Hg}}\right)\left(\frac{1460°\text{R}}{492°\text{R}}\right) = \frac{13{,}160 \text{ ft}^3 \text{ flue gas}}{\text{min}}$$

The statement of the method of solution presented above is intended to be as straightforward as possible in the verbal sense. It is verbally convenient to stay on one basis throughout the problem but it is mathematically convenient to shift bases for certain parts of the calculations. Therefore the verbal solutions of succeeding problems will indicate the changing of basis whenever it is mathematically desirable to do so.

Example 6-8. A steam boiler is fired with a coal having the following analyses:

Ultimate		*Proximate*	
C	60%w	FC	40%w
H	14	VCM	41
O	16	Moisture	9
N	0	Ash	10
S	0		
Ash	10		

Seventeen thousand eight hundred and sixty cubic feet of wet air is supplied per 100 lb of coal fired. The wet air is at 750 mm Hg, 60°F, and the water vapor in it exerts a partial pressure of 10 mm Hg.

The dry refuse from this furnace contains 11.2% FC, 9.3% VCM, and 79.5% ash. Because of poor operation, only 80% of the carbon burned forms CO_2; the rest forms CO.

Calculate the following:

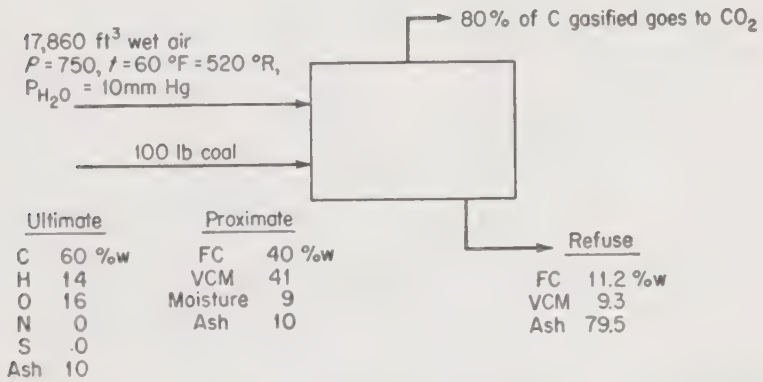
a. Per cent excess air

b. The Orsat analysis of the flue gas

c. The partial pressure of water vapor in the wet flue gas, if the total pressure is 750 mm Hg

d. An over-all material balance, in pounds

Method. First draw a diagram and indicate known quantities:



Basis: 100 lb coal fired. Calculate the moles of oxygen required to burn completely all the combustible fired. Calculate the oxygen (and nitrogen) supplied and then the per cent excess air (part *a*). By an ash balance determine the FC and VCM lost. Calculate the percentage of carbon in the VCM from the coal analyses, and then the carbon lost in the VCM. Since the total amount of carbon fired is known, the carbon gasified can be determined. Eighty per cent of it forms CO_2 and the rest forms CO. From the ultimate analysis of the coal, calculate the

hydrogen equivalent to oxygen and then the net hydrogen. The fraction of net hydrogen burned is the same as the fraction of VCM burned, and therefore the oxygen consumed by the net hydrogen may be computed. Subtract the oxygen in CO_2 and CO, plus that combined with net hydrogen, from the oxygen supplied to determine the amount of unconsumed oxygen in the flue gas. The amount of nitrogen supplied was computed in part *a*. Compute the analysis of the dry flue gas (part *b*).

Determine the amount of water entering with the wet air. Compute the combined water in the coal from the two coal analyses. The fraction of combined water gasified is the same as the fraction of the VCM gasified. All the coal moisture is gasified. Add the water quantities and calculate the partial pressure of the water in the wet flue gas (part *c*). Calculate the weights of entering and leaving streams and write the over-all material balance (part *d*).

Solution

a. Per cent excess air

Basis: 100 lb coal fired

Compound	lb	Mole	Mole O_2 required
C	60	5	5
H_2	14	7	3.5
O_2	16	0.5	−0.5
Ash	10		
	100		8 mole O_2 required

$$\left[(17{,}860 \text{ ft}^3 \text{ dry air})\left(\frac{740}{760}\right)\left(\frac{492}{520}\right)\right]\left(\frac{\text{mole dry air}}{359 \text{ ft}^3 \text{ dry air}}\right) = 45.8 \text{ mole dry air supplied}$$

$$(45.8 \text{ mole dry air})\left(\frac{0.21 \text{ mole } O_2}{\text{mole dry air}}\right) = 9.62 \text{ mole } O_2 \text{ supplied}$$

$$45.8 - 9.6 = 36.2 \text{ mole } N_2 \text{ supplied}$$

$$9.62 - 8.0 = 1.62 \text{ mole } O_2 \text{ in excess}$$

$$\left(\frac{1.62 \text{ mole } O_2 \text{ excess}}{8 \text{ mole } O_2 \text{ required}}\right)(100) = 20.3\% \text{ excess air} \qquad \text{(part } a\text{)}$$

b. The Orsat analysis of the flue gas

$$(10 \text{ lb ash})\left(\frac{0.112 \text{ lb FC lost}}{0.795 \text{ lb ash}}\right) = 1.410 \text{ lb FC lost in refuse}$$

$$(10 \text{ lb ash})\left(\frac{0.093 \text{ lb VCM lost}}{0.795 \text{ lb ash}}\right) = 1.169 \text{ lb VCM lost in refuse}$$

$$(1.169 \text{ lb VCM})\left(\frac{20 \text{ lb C}}{41 \text{ lb VCM}}\right)$$

$$= 0.571 \text{ lb C lost in VCM} \qquad \text{(from coal analyses)}$$

$$1.410 + 0.571 = 1.981 \text{ lb C lost in refuse}$$

$$60 \text{ lb C fired} - 1.981 = 58.02 \text{ lb C gasified} \approx 4.84 \text{ mole}$$

$$(4.84 \text{ mole C})\left(\frac{0.2 \text{ mole C} \rightarrow \text{CO}}{\text{mole C gasified}}\right) = 0.968 \text{ mole CO formed}$$

$$4.84 - 0.97 = 3.87 \text{ mole } CO_2 \text{ formed}$$

$$(16 \text{ lb } O_2 \text{ in } 100 \text{ lb coal})\left(\frac{2 \text{ lb } H_2}{16 \text{ lb } O_2}\right)$$

$$= 2 \text{ lb } H_2 \text{ in moisture and combined water}$$

$$14 \text{ lb total } H_2 - 2 \text{ lb } H_2 = 12 \text{ lb net } H_2$$

$$(12 \text{ lb net } H_2 \text{ charged})\left(\frac{1.169 \text{ lb VCM lost}}{41 \text{ lb VCM fired}}\right)$$

$$= 0.342 \text{ lb net } H_2 \text{ lost in refuse}$$

$$12 - 0.34 = 11.66 \text{ lb net } H_2 \text{ burned} \approx 5.83 \text{ mole net } H_2 \text{ burned}$$

Oxygen consumed = O_2 to form CO + O_2 to form CO_2 + O_2 to form H_2O = $(0.968 \text{ mole CO})\left(\frac{0.5 \text{ mole } O_2}{\text{mole CO}}\right) + (3.87 \text{ mole } CO_2)\left(\frac{1 \text{ mole } O_2}{\text{mole } CO_2}\right)$

$$+ (5.83 \text{ mole } H_2)\left(\frac{0.5 \text{ mole } O_2}{\text{mole } H_2}\right) = 0.484 + 3.87 + 2.91$$

$$= 7.26 \text{ mole } O_2 \text{ consumed}$$

$$9.62 \text{ mole } O_2 \text{ supplied} - 7.26 \text{ mole } O_2 \text{ consumed}$$

$$= 2.36 \text{ mole } O_2 \text{ unconsumed}$$

Dry flue gas/100 lb coal

Compound	Mole	%m
CO_2	3.87	8.90
CO	0.968	2.23
O_2	2.36	5.43
N_2	36.20	83.44
	43.40	100.00

(part *b*)

c. p_{H_2O} in wet flue gas

$$(9.62 \text{ mole } O_2 \text{ supplied})\left(\frac{100 \text{ mole dry air}}{21 \text{ mole } O_2}\right)\left(\frac{10 \text{ mole } H_2O}{740 \text{ mole dry air}}\right)$$

$$= 0.619 \text{ mole } H_2O \text{ in wet air}$$

16 lb O_2 in combined H_2O and moisture

$\approx$ 18 lb total H_2O therefore, 9 lb combined H_2O

6.0 mole H_2O equivalent to net H_2 + 0.5 mole combined H_2O
= 6.5 mole H_2O possible from net H_2 and combined H_2O in VCM

$$(6.5 \text{ mole equivalent } H_2O)\left(\frac{1.169 \text{ lb VCM lost}}{41 \text{ lb VCM fired}}\right)$$

= 0.1852 mole equivalent H_2O lost

6.5 − 0.185 = 6.31 mole H_2O in flue gas from net H_2 and combined H_2O gasified

9 lb moisture ≈ 0.5 mole moisture gasified

Total H_2O in flue gas = water in air + moisture in coal
+ water equivalent to net H_2 and combined H_2O gasified
= 0.619 mole H_2O + 0.5 mole H_2O + 6.31 mole H_2O
= 7.43 mole H_2O in wet flue gas

43.40 mole dry flue gas (see *b*) + 7.43 mole H_2O = 50.83 mole wet flue gas

$$(750 \text{ mm Hg})\left(\frac{7.43 \text{ mm } H_2O}{50.83 \text{ mole wet flue gas}}\right) = 109.7 \text{ mm Hg}$$

p_{H_2O} is 109.7 mm Hg (part *c*).

d. Over-all material balance

Basis: 100 lb of coal as fired

Weight of wet air:

$$(45.8 \text{ mole dry air})\left(\frac{28.9 \text{ lb dry air}}{\text{mole dry air}}\right) = 1324 \text{ lb}$$

$$(0.619 \text{ mole } H_2O)\left(\frac{18 \text{ lb } H_2O}{\text{mole } H_2O}\right) = \frac{11.12 \text{ lb}}{1335 \text{ lb}}$$

Weight of refuse:

1.410 lb FC + 1.169 lb VCM + 10 lb ash = 12.58 lb

Weight of flue gas:

Compound	Mole	MW	lb
CO_2	3.87	44	170.0
CO	0.968	28	27.1
O_2	2.36	32	75.5
N_2	36.20	28	1014.0
H_2O	7.43	18	133.7
	50.83		1420.3

Material balance:

In		Out	
100 lb coal +	1335 lb wet air	= 13 lb refuse +	1420 lb wet flue gas
	1435	=	1433

This is an unusually close check. Discrepancies of about 2% are not uncommon in such balances. The discrepancy is usually caused by the

fact that the oxygen content of the coal is determined by difference so that any errors in the various parts of the coal analysis result in an erroneous figure for the oxygen.

Example 6-9. The coal of Example 6-8 has a heating value of 16,000 Btu/lb. The flue gases leave at 496°F. Feedwater to the steam boiler is at 102°F. The steam produced is at 150 psig and saturated. Nine hundred and thirty-nine pounds of steam are produced per 100 lb of coal. Calculate the following:

a. The percentage of the heating value of the coal lost because of unburned combustible in the refuse

b. The percentage of the heating value of the coal lost because of unburned combustible in the flue gases

c. The percentage of the heating value of the coal lost because of sensible and latent heat in the flue gases

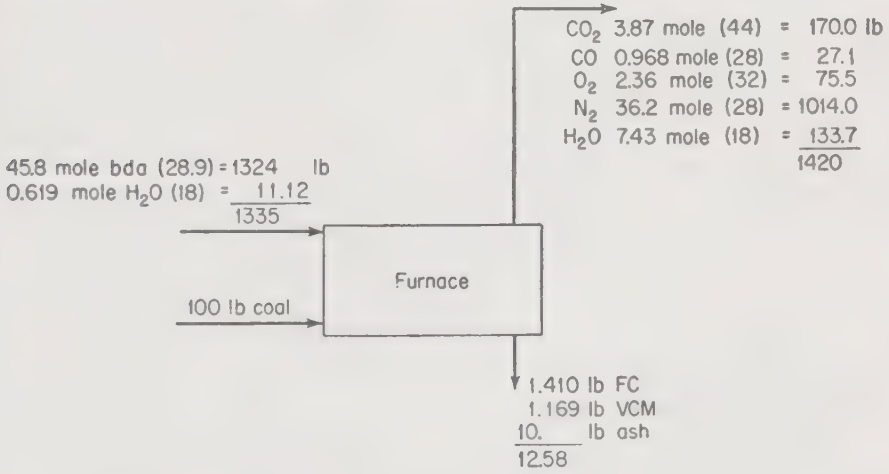
d. The percentage of the heating value of the coal which goes to raise steam

e. A complete over-all heat balance

f. The percentage of the heating value of the coal lost through radiation and unaccounted-for losses

Solution

Take as a datum 60°F, water in the liquid state. First draw a diagram indicating the material-balance results of Example 6-8.



a. Heating value lost in refuse: HV of VCM

Basis: 1 lb of coal

$$(0.4 \text{ lb C})(14{,}550) = 5820 \text{ Btu from C}$$

$$16{,}000 - 5820 = \frac{10{,}180 \text{ Btu}}{0.41 \text{ lb VCM}}$$

Therefore,
$$\frac{10{,}180}{0.41} = \frac{24{,}800 \text{ Btu}}{\text{lb VCM}}$$
$$(1.410 \text{ lb C})(14{,}550) = 20{,}500$$
$$(1.169 \text{ lb VCM})(24{,}800) = 29{,}000$$
$$49{,}500 \text{ Btu total loss}$$
$$\frac{(49{,}500)(100)}{(16{,}000)(100)} = 3.10\% \text{ loss}$$

b. Heating value lost because of CO loss

$$(0.968 \text{ mole CO})\left(\frac{68{,}000 \text{ cal}}{\text{gmole}}\right)\left(\frac{1.8 \text{ (Btu)(gmole)}}{\text{(lbmole)(cal)}}\right) = 118{,}500 \text{ Btu}$$
$$\frac{(118{,}500)(100)}{(16{,}000)(100)} = 7.40\% \text{ loss}$$

c. Heating value lost because of sensible and latent heat in flue gases

Sensible heat:

Compound	Mole	Mean C_p between 0°F and 496°F; Btu/(mole)(F°)	Btu/F°
CO_2	3.87	9.72	37.6
CO	0.968	7.03	6.80
O_2	2.36	7.20	17.00
N_2	36.2	7.03	254.00
H_2O	7.43	8.19	60.8
			376.2

$$(376.2)\left(\frac{\text{Btu}}{\text{F°}}\right)(496 - 60)(\text{F°}) = 163{,}800 \text{ Btu}$$

Latent heat:

$$(7.43 \text{ mole } H_2O)\left(\frac{18 \text{ lb } H_2O}{\text{mole } H_2O}\right)\left(\frac{1060 \text{ Btu}}{\text{lb } H_2O}\right) = 142{,}000 \text{ Btu}$$
$$163{,}800 + 142{,}000 = 305{,}800 \text{ Btu}$$
$$\frac{(305{,}800)(100)}{(16{,}000)(100)} = 19.1\% \text{ loss}$$

d. Heat which goes to raise steam

From Appendix C,

$$\text{Heat in feedwater (102°F) above } H_2O \text{ at 32°F} = \frac{70.0 \text{ Btu}}{\text{lb}}$$
$$\text{Heat in saturated steam at 150 psig above } H_2O \text{ at 32°F} = \frac{1195.5 \text{ Btu}}{\text{lb}}$$
$$\text{Heat added/lb steam} = 1195.5 - 70 = 1125.5 \text{ Btu}$$
$$(939 \text{ lb steam})\left(\frac{1125.5 \text{ Btu}}{\text{lb}}\right) = 1{,}057{,}000 \text{ Btu}$$
$$\frac{(1{,}057{,}000)(100)}{(16{,}000)(100)} = 66\%$$

e. Over-all heat balance
Basis: 100 lb coal

Heat in, in coal:

Since the coal is fired at room temperature, its sensible heat may be neglected. The adsorbed moisture on the coal is, for practical purposes, at the datum plane also. Therefore the only heat input in the coal stream is potential heat.

$$(100 \text{ lb coal}) \left(\frac{16{,}000 \text{ Btu}}{\text{lb coal}}\right) = 1{,}600{,}000 \text{ Btu}$$

Heat in, in air:

The air is supplied at 60°F; therefore the sensible heat in the dry air and water vapor is zero.

The latent heat supplied in water vapor is

$$(0.619 \text{ mole water vapor}) \left(\frac{18 \text{ lb } H_2O}{\text{mole } H_2O}\right) \left(\frac{1060 \text{ Btu}}{\text{lb } H_2O}\right) = 11{,}810 \text{ Btu}$$

Heat in, in feedwater:

$$(939 \text{ lb } H_2O) \left(\frac{1 \text{ Btu}}{(\text{lb})(\text{F°})}\right) (102 - 60)(\text{F°}) = 39{,}400 \text{ Btu}$$

Heat out, in refuse:

The quantity of refuse is so small that its sensible-heat content may be neglected.

The loss in refuse is potential heat and, as already shown, amounts to 49,500 Btu.

Heat out, in flue gases: As shown in parts *b* and *c*,

$$118{,}500 \text{ Btu} + 305{,}800 \text{ Btu} = 424{,}300 \text{ Btu}$$

Heat out, in steam: From Appendix E,

$$\text{Heat in } H_2O \text{ at } 60°\text{F above } H_2O \text{ at } 32°\text{F} = \frac{28 \text{ Btu}}{\text{lb}}$$

$$\text{Heat in saturated steam at 150 psig above } H_2O \text{ at } 32°\text{F} = \frac{1195.5 \text{ Btu}}{\text{lb}}$$

$$\text{Heat in steam above } H_2O \text{ at } 60°\text{F} = 1195.5 - 28 = 1167.5$$

$$(939 \text{ lb steam})(1167.5) = 1{,}095{,}000 \text{ Btu}$$

Over-all balance:

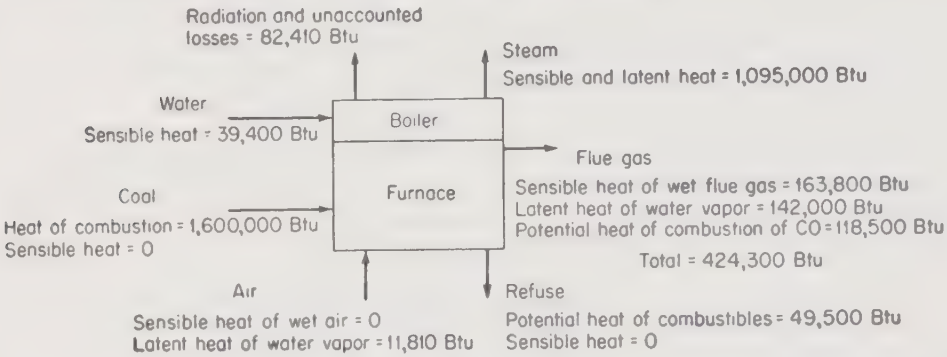
$$\underset{\text{In}}{1{,}600{,}000 + 11{,}810 + 39{,}400} = \underset{\text{Out}}{49{,}500 + 424{,}300 + 1{,}095{,}000 + \text{radiation and unaccounted-for losses}}$$

f. The percentage of the heating value of the coal lost through radiation and unaccounted-for losses

$$\text{Radiation and unaccounted-for losses} = 82{,}410 \text{ Btu}$$

$$\frac{(82{,}410)(100)}{(16{,}000)(100)} = 5.15\%$$

The following diagram indicates the heat quantities:


Radiation and unaccounted losses = 82,410 Btu
Steam
Sensible and latent heat = 1,095,000 Btu
Water
Sensible heat = 39,400 Btu
Boiler
Flue gas
Coal
Furnace
Sensible heat of wet flue gas = 163,800 Btu
Latent heat of water vapor = 142,000 Btu
Potential heat of combustion of CO = 118,500 Btu
Heat of combustion = 1,600,000 Btu
Sensible heat = 0
Total = 424,300 Btu
Air
Refuse
Sensible heat of wet air = 0
Latent heat of water vapor = 11,810 Btu
Potential heat of combustibles = 49,500 Btu
Sensible heat = 0

Most industrial furnaces are used to raise steam. There are, therefore, many designs for "boilers" in which the primary concern is for efficient transfer of heat from the flue gases to boiling water. The over-all efficiency of such a plant may be expressed as the percentage of the heating value of the fuel that goes into the feedwater in order to form the steam. This efficiency depends on the design and size of the furnace, on the care taken in operating it, and on the type and quality of fuel used. The efficiency of industrial units varies from about 70 to about 85%. Most of the heat which is lost is lost as sensible heat in the flue gases.

OXIDATION OF SULFUR AND SULFUR COMPOUNDS

Oxidation of Sulfur. Sulfur and sulfide ores are burned with air in specially constructed furnaces in order to make sulfur dioxide and sulfur trioxide.

When sulfur is burned, the following reactions occur:

$$S + O_2 \rightarrow SO_2$$
$$S + 1.5O_2 \rightarrow SO_3$$

Normally only a few per cent of the sulfur charged to the burner is oxidized to SO_3. The stoichiometric relationships may be illustrated as follows:

Example 6-10. Five hundred pounds per hour of pure sulfur is burned with 20% excess air (*based on conversion to* SO_2). Five per cent of the

sulfur is oxidized to SO_3 and 95% to SO_2. The air is dry. Calculate the composition (in %m) of the gas leaving the burner.

Solution

Basis: 1 hr

$$(500 \text{ lb S})\left(\frac{\text{mole}}{32 \text{ lb}}\right) = 15.62 \text{ mole S}$$

$$(15.62 \text{ mole S})\left(\frac{1 \text{ mole } O_2 \text{ theoretically required}}{\text{mole S}}\right)\left(\frac{1.2 \text{ mole } O_2 \text{ supplied}}{\text{mole } O_2 \text{ theoretically required}}\right) = 18.75 \text{ mole } O_2 \text{ supplied}$$

$$(18.75 \text{ mole } O_2 \text{ supplied})\left(\frac{79 \text{ mole } N_2 \text{ supplied}}{21 \text{ mole } O_2 \text{ supplied}}\right) = 70.60 \text{ mole } N_2$$

$$(15.62 \text{ mole S})\left(\frac{0.05 \text{ mole } SO_3 \text{ formed}}{\text{mole S}}\right) = 0.781 \text{ mole } SO_3 \text{ formed}$$

$$15.62 \text{ mole S} - 0.781 \text{ mole S in } SO_3 = 14.84 \text{ mole } SO_2$$

$$(14.84 \text{ mole } SO_2)\left(\frac{1 \text{ mole } O_2 \text{ consumed}}{\text{mole } SO_2}\right) = 14.84 \text{ mole } O_2 \text{ consumed for } SO_2$$

$$(0.781 \text{ mole } SO_3)\left(\frac{1.5 \text{ mole } O_2 \text{ consumed}}{\text{mole } SO_3}\right) = 1.171 \text{ mole } O_2 \text{ consumed for } SO_3$$

$$14.48 + 1.171 = 16.01 \text{ mole } O_2 \text{ consumed for S combustion}$$

$$18.75 \text{ mole } O_2 \text{ supplied} - 16.01 \text{ mole } O_2 \text{ consumed} = 2.74 \text{ mole } O_2 \text{ unconsumed}$$

Compound	Mole	Composition in mole %
SO_2	14.84	16.70
SO_3	0.781	0.88
O_2	2.74	3.08
N_2	70.60	79.40
	88.96	100.06

Analysis of Combustion Gases. Gases from the combustion of sulfur or sulfide ores are analyzed by the Orsat method. A sample is collected over mercury, a drop of water being placed on the mercury to ensure saturation of the gas sample with water vapor. (If the sample were only partly saturated with water vapor, the conclusion that the Orsat analysis is on a dry basis would not hold.) The water effectively removes SO_3.

The Orsat analysis of the gas formed in Example 6-10 would be calculated as follows:

Compound	Mole	%m
SO_2	14.84	16.85
O_2	2.74	3.11
N_2	70.60	80.04
	88.18	100.00

The gas analysis does not measure the total composition of the dry combustion gases because SO_3 is undetermined. However, the amount of SO_3 formed may be calculated from the analysis because the ratio of oxygen to nitrogen found by gas analysis differs from the ratio in the air supplied by the amount of oxygen converted to SO_3 per mole of nitrogen. In the case of a sulfur burner or a sulfur dioxide converter all the SO_3 formed leaves with the other gases. When sulfur compounds are burned, SO_3 is often discharged with the refuse (adsorbed), and a refuse analysis is required when burner-gas composition is to be calculated. The *composition* of the dry combustion gases of Example 6-10 would be calculated from the gas *analysis* like this:

Basis: 100 mole of SO_3-free gas

Compound	*Mole*
SO_2	16.85
O_2	3.11
N_2	80.04
	100.00

$$(80.04 \text{ mole } N_2 \text{ supplied}) \left(\frac{21 \text{ mole } O_2}{79 \text{ mole } N_2}\right) = 21.25 \text{ mole } O_2 \text{ supplied}$$

$$16.85 \text{ mole } O_2 \text{ in } SO_2 + 3.11 \text{ mole } O_2 = 19.96 \text{ mole } O_2 \text{ "appearing"}$$

$$21.25 - 19.96 = 1.29 \text{ mole } O_2 \text{ disappeared}$$

Therefore, 1.29 mole O_2 has been converted to SO_3.

$$(1.29 \text{ mole } O_2) \left(\frac{1 \text{ mole } SO_3}{1.5 \text{ mole } O_2}\right) = 0.86 \text{ mole } SO_3 \text{ formed}$$

The composition of the dry gases is therefore as follows:

Compound	Mole	%m
SO_3	0.86	0.85
SO_2	16.85	16.70
O_2	3.11	3.08
N_2	80.04	79.40
	100.86	100.03

The accuracy of the values determined by this method depends on the percentage conversion of the sulfur to SO_3. Since oxygen disappearance is the small difference between two large numbers when little SO_3 is formed, results can be inexact in such a case. (Compare with the composition calculated in Example 6-10.)

When SO_3 is desired (for instance, for sulfuric acid manufacture), the burner gases are fed to catalyst chambers where the dioxide is converted to the trioxide. Oxygen disappearance is again the clue to SO_3 production, but sulfur disappearance also occurs and can be calculated as a check. Examine the solution to the following example.

Example 6-11. The gases from a sulfur-compound burner have the following analysis: 9.86% SO_2, 8.54% O_2, 81.60% N_2. After passage of the gases through a catalytic converter, the analysis is 0.605% SO_2, 4.50% O_2, and 94.9% N_2.

What percentage of the SO_2 entering the converter has been oxidized to SO_3?

Solution

Basis: 100 mole of entering SO_3-free DBG (dry burner gas). (The analysis is on this basis.)

$$SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3$$

(81.60 mole N_2 entering and leaving)

$$\left(\frac{\text{100 mole } SO_3\text{-free DCG (dry converter gas)}}{\text{94.9 mole } N_2 \text{ leaving}}\right) = 86.0 \text{ mole } SO_3\text{-free DCG leaving}$$

Compound	%m	Mole
SO_2	0.605	0.52
O_2	4.50	3.87
N_2	94.90	81.60
		85.99

8.54 mole uncombined O_2 enters but only 3.87 mole leaves

$$8.54 - 3.87 = 4.67 \text{ mole of } O_2 \text{ reacting with } SO_2$$

$$(4.67 \text{ mole } O_2)\left(\frac{\text{1 mole } SO_3 \text{ formed from } SO_2}{\text{0.5 mole } O_2}\right) = 9.34 \text{ mole } SO_3 \text{ formed}$$

Check:

Mole S per 100 mole SO_3-free DBG = 9.86

Mole S per equivalent mole leaving SO_3-free DCG = 0.52

$9.86 - 0.52 = 9.34$ mole SO_3 formed

$$\left(\frac{\text{9.34 mole } SO_3 \text{ formed}}{\text{9.86 mole } SO_2 \text{ entering}}\right)(100) = 94.6\% \text{ of entering } SO_2 \text{ converted to } SO_3$$

Note: The analyses give us the proportions of materials but not the quantities. In order to determine oxygen disappearance or sulfur disappearance, a basis must be chosen. Since all the entering nitrogen leaves, a nitrogen balance is used to determine what quantity of leaving gas is equivalent (because it contains the same amount of nitrogen) to the 100 mole of entering gas chosen as the basis of calculations. A different basis might be chosen (such as 100 mole of leaving SO_3-free DCG gas), but the nitrogen balance would still be necessary to relate the quantities.

The total composition of the DCG or DBG cannot be calculated from the information given. It would be necessary to state the distribution of SO_3 between refuse and DBG if total compositions were requested.

Oxidation of Sulfide Ores. Iron pyrites (pronounced "pie-rye-tease") is the sulfide ore most commonly burned for sulfur dioxide manufacture. It contains iron sulfide (FeS_2), small amounts of other metallic sulfides, and appreciable amounts of totally incombustible materials. The incombustibles are reported as "gangue" in the analysis. The primary considerations and techniques for sulfide-ore-burner calculations may be shown by means of examples based on ores containing only FeS_2 and gangue. The principal reactions are

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$
$$4FeS_2 + 15O_2 \rightarrow 2Fe_2O_3 + 8SO_3$$

Loss of Sulfur in the Refuse. All the gangue and iron are in the refuse. The iron is chiefly the trivalent oxide (Fe_2O_3). Some unburned FeS_2 may be present, and a small amount of the divalent oxide is possible. This latter is small enough to be neglected in a well-operated furnace. It can be determined by analysis if necessary. The main sulfur compounds in the refuse are SO_3, which is adsorbed on the cinder, and unburned FeS_2. The total SO_3 formed may be computed from the gas analysis. If the quantity of SO_3 in the refuse (determined by analysis) be subtracted from the total, the burner-gas composition can be determined.

Examples of the two types of sulfur loss are given below.

Example 6-12. The cinder from the combustion of iron pyrites containing 85%w FeS_2 and 15%w gangue carries 1% S as FeS_2. How many pounds of FeS_2 are lost in the cinder per 100 lb of pyrites fired?

Solution

Basis: 100 lb pyrites fired. The reactions are

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$
$$4FeS_2 + 15O_2 \rightarrow 2Fe_2O_3 + 8SO_3$$

Let X = lb FeS_2 lost.

$$(X \text{ lb } FeS_2)\left(\frac{64 \text{ lb S}}{120 \text{ lb } FeS_2}\right) = \left(\frac{64}{120}\right)(X) \text{ lb S lost}$$

$$85 - X = \text{lb } FeS_2 \text{ burned}$$

$$(85 - X)\text{lb } FeS_2 \text{ burned}\left(\frac{160 \text{ lb } Fe_2O_3 \text{ formed}}{240 \text{ lb } FeS_2 \text{ burned}}\right)$$

$$= \frac{(85 - X)(160) \text{ lb } Fe_2O_3 \text{ formed}}{240}$$

$$\text{lb cinder} = 15 \text{ lb gangue} + \frac{(85 - X)(160) \text{ lb } Fe_2O_3}{240} + X \text{ lb } FeS_2$$

$$\frac{64X \text{ lb S lost}}{120} = \left(\frac{1 \text{ lb S}}{100 \text{ lb cinder}}\right)(\text{lb cinder})$$

$$\frac{64X}{120} = (0.01)\left[15 + \frac{(85 - X)160}{240} + X\right]$$

$$X = 1.352 \text{ lb } FeS_2 \text{ lost}$$

Example 6-13. The cinder from the combustion of iron pyrites containing 85%w FeS_2 and 15%w gangue carries 1% S as SO_3.

How many pounds of SO_3 are lost in the cinder per 100 lb of pyrites charged?

Solution

Basis: 100 lb pyrites charged. Equations:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$
$$4FeS_2 + 15O_2 \rightarrow 2Fe_2O_3 + 8SO_3$$

$$(85 \text{ lb } FeS_2 \text{ burned})\left(\frac{160 \text{ lb } Fe_2O_3 \text{ formed}}{240 \text{ lb } FeS_2 \text{ burned}}\right) = 56.7 \text{ lb } Fe_2O_3 \text{ formed}$$

$$56.7 \text{ lb } Fe_2O_3 + 15 \text{ lb gangue} = 71.7 \text{ lb of } SO_3\text{-free cinder}$$

Basis: 100 lb cinder

$$(1 \text{ lb S})\left(\frac{80 \text{ lb } SO_3}{32 \text{ lb S}}\right) = 2.5 \text{ lb } SO_3 \approx 2.5\% \text{ } SO_3$$

Basis: 100 lb pyrites charged

$$(71.7 \text{ lb } SO_3\text{-free cinder})\left(\frac{2.5 \text{ lb } SO_3}{97.5 \text{ lb } SO_3\text{-free cinder}}\right) = 1.839 \text{ lb } SO_3 \text{ lost}$$

Deductions from the Gas Analysis. The amount of SO_3 formed can be calculated from the Orsat analysis of the sulfide-ore-burner gases if it is remembered that oxygen disappearance is now caused by two phenomena. The first is SO_3 formation, and the other is iron oxide formation. Since

all the SO_2 formed "appears" in the burner gases, the total oxygen that reacted with FeS_2 to form SO_2 and Fe_2O_3 can be computed. If this oxygen "accounted for" in SO_2 formation plus the uncombined oxygen be subtracted from the oxygen equivalent to nitrogen, the remainder is oxygen that burned FeS_2 to Fe_2O_3 and SO_3. The calculation is shown below.

Example 6-14. An analysis of the burner gases from combustion of iron pyrites shows 10% SO_2 and 5% O_2. What percentage of the sulfur burned is oxidized to SO_3?

Solution

Basis: 100 mole SO_3-free DBG. Equations:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$
$$4FeS_2 + 15O_2 \rightarrow 2Fe_2O_3 + 8SO_3$$

$$(10 \text{ mole } SO_2)\left(\frac{11 \text{ mole } O_2}{8 \text{ mole } SO_2}\right)$$
$$= 13.75 \text{ mole } O_2 \text{ "accounted for" in } SO_2 \text{ formation}$$

$$(85 \text{ mole } N_2)\left(\frac{21 \text{ mole } O_2}{79 \text{ mole } N_2}\right) = 22.6 \text{ mole } O_2 \text{ supplied}$$

$$22.6 \text{ mole } O_2 - 13.75 \text{ mole } O_2 - 5 \text{ mole } O_2 \text{ uncombined}$$
$$= 3.85 \text{ mole } O_2 \text{ consumed in } SO_3 \text{ formation}$$

$$(3.85 \text{ mole } O_2)\left(\frac{8 \text{ mole } SO_3}{15 \text{ mole } O_2}\right) = 2.055 \text{ mole } SO_3 \text{ formed}$$

Therefore,

$$\text{Total S burned per 100 mole } SO_3\text{-free DBG} = 10 \text{ mole S to } SO_2$$
$$+ 2.055 \text{ mole S to } SO_3 = 12.055 \text{ mole S}$$

$$\left(\frac{2.055}{12.055}\right)(100) = 17\% \text{ of S burned is oxidized to } SO_3$$

The "gangue + Fe_2O_3" balance of Example 6-13 and the oxygen balance of Example 6-14 provide the information necessary to obtain the quantities of the various streams on the same basis, as shown next.

Example 6-15. Seven hundred pounds per hour of iron pyrites containing 85%w FeS_2 and 15%w gangue are charged to a burner. The cinder contains 1% S as SO_3. The burner-gas analysis shows 10% SO_2 and 5% O_2. Air used for combustion is dry. How many cubic feet of total burner gases at 1 atm and 60°F are produced per hour?

Solution

Basis: 1 hr of operation

$$(700 \text{ lb pyrites})\left(\frac{85 \text{ lb } FeS_2}{100 \text{ lb pyrites}}\right)\left(\frac{64 \text{ lb S}}{120 \text{ lb } FeS_2}\right)$$
$$= 317 \text{ lb S charged and burned}$$

(From Example 6-13)

$$(700 \text{ lb pyrites})\left(\frac{1.839 \text{ lb } SO_3 \text{ lost}}{100 \text{ lb pyrites}}\right)\left(\frac{32 \text{ lb S}}{80 \text{ lb } SO_3}\right) = 5.15 \text{ lb S lost}$$

$$317 - 5.15 = 311.85 \text{ lb S in burner gases}$$

(From Example 6-14)

$$\left(\frac{12.055 \text{ mole S burned}}{100 \text{ mole } SO_3\text{-free DBG}}\right)\left(\frac{311.85 \text{ mole S in burner gas}}{317 \text{ mole S burned}}\right) = \frac{11.86 \text{ mole S in burner gas}}{100 \text{ mole } SO_3\text{-free burner gas}}$$

$$11.86 - 10 \text{ mole S in } SO_2 = 1.86 \text{ mole S in } SO_3$$

Therefore, 101.86 mole total burner gas is formed per 11.86 mole S in burner gas.

$$(311.85 \text{ lb S in burner gas})\left(\frac{\text{mole S}}{32 \text{ lb S}}\right)\left(\frac{101.86 \text{ mole total BG}}{11.86 \text{ mole S}}\right) = 83.5 \text{ mole total BG}$$

$$\left[(83.5 \text{ mole total BG})\left(\frac{359 \text{ ft}^3}{\text{mole}}\right)\right]\left(\frac{520}{492}\right) = \frac{31{,}700 \text{ ft}^3}{\text{hr}}$$

Sulfuric Acid Manufacture. In the manufacture of sulfuric acid by the contact process, catalytic oxidation of SO_2 is accomplished under appropriate conditions in equipment known as a converter. The reaction is $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$. Two or more converters may be in series, and extra air (called "secondary air") may be supplied. The SO_3 is absorbed by countercurrent passage of the gases (upward) and absorbing liquid (downward) in ceramic-packed towers.

Sulfuric acid is formed by the reaction $SO_3 + H_2O \rightarrow H_2SO_4$. The absorption cannot be satisfactorily accomplished by water alone, because the vapor pressure of water is sufficiently high to cause formation of an acid mist which hinders absorption. The partial pressure of water above a sulfuric acid solution depends on the concentration of the acid. Sulfuric acid solutions of a concentration between 98.5%w and 99%w exert a lower partial pressure of water than do solutions of higher or lower concentration. It is customary to feed 98.5 to 99%w acid to the top of an absorption tower, which discharges a 20% oleum product. (An oleum is a solution of SO_3 in H_2SO_4. Twenty per cent oleum is 20 lb SO_3/80 lb H_2SO_4.) The gases from the top of the first absorption tower pass up a second tower that discharges 98%w acid. Part of the 98%w acid is fed to the first tower, and part of it is diluted and recycled to the top of the second tower. Contact plants are now quite standardized and virtually automatic. We have taken the liberty of considering different acid strengths in some of our problems.

Example 6-16. Two hundred and fifty pounds per hour of 98%w H_2SO_4 enters an absorption tower of a contact sulfuric acid plant. If 20% oleum is produced in this tower, how many pounds per hour of SO_3 are absorbed?

Solution

Basis: 1 hr. Let X = lb of SO_3 absorbed. Equation:

$$H_2O + SO_3 \rightarrow H_2SO_4$$

$$\begin{array}{c} SO_3 \text{ in} \qquad\qquad SO_3 \text{ out} \\ \text{As } H_2SO_4 + SO_3 \text{ absorbed} = SO_3 \text{ in 20\% oleum} \end{array}$$

$$(250 \text{ lb 98\%w acid})\left(\frac{98 \text{ lb } H_2SO_4}{100 \text{ lb 98\%w acid}}\right)\left(\frac{80 \text{ lb } SO_3}{98 \text{ lb } H_2SO_4}\right) + X$$

$$= (250 + X)\text{lb 20\% oleum}\ \frac{[20 + (^{8}\%_{98})80] \text{ lb } SO_3}{100 \text{ lb 20\% oleum}}$$

$$X = 90.3 \text{ lb } SO_3 \text{ absorbed}$$

Do the following problems (Examples 6-17, 6-18, and 6-19) and then compare your solutions with those given.

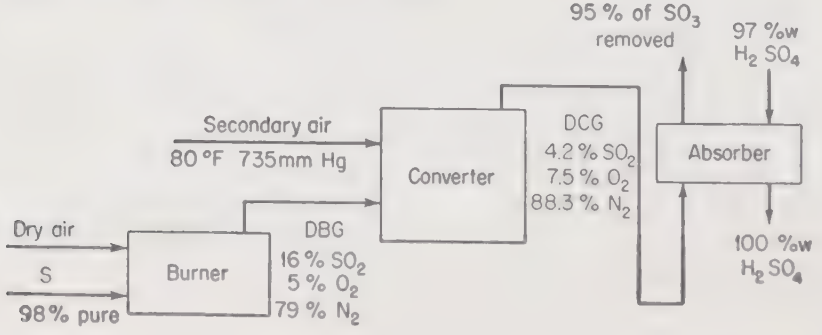
Example 6-17. A sulfur burner, burning sulfur of 98% purity with dry air, discharges gas at 1300°F containing 16% SO_2, 5% O_2, and 79% N_2. Both the sulfur and the air are supplied at 80°F. The heat of combustion of sulfur to SO_2 is 127,690 Btu/mole at 25°C. The burner gas is mixed with more dry air (called "secondary air") and passed through a converter. Analysis of the converter gas shows 4.2% SO_2, 7.5% O_2, and 88.3% N_2. An absorber subsequently removes 95% of the SO_3 in the converter gas by absorbing it in 97% H_2SO_4 to produce 100% H_2SO_4. No SO_3 is formed in the absorber.

a. Calculate the volume of secondary air supplied at 80°F and 735 mm Hg per 100 lb impure sulfur entering.

b. How many pounds of 97% H_2SO_4 must be supplied per 100 mole of SO_3-free converter gas?

c. What percentage of the heat generated in the burner leaves as sensible heat in the burner gas?

Method. Draw a diagram and label it.



On the basis of 100 mole of SO_3-free DCG, calculate the oxygen consumed in SO_3 formation and the amount of SO_3 formed. The mole SO_3 formed plus the mole SO_2 present is the total sulfur in the DCG. This must all have entered in the DBG. Pick a basis of 100 mole of SO_3-free DBG. The analysis shows that no SO_3 was formed in the burner; therefore the 16 mole S in SO_2 is all the sulfur in the DBG. Calculate the amount of nitrogen associated with 16 mole total S in DCG. Subtract the DBG nitrogen from the DCG nitrogen to obtain the nitrogen supplied in secondary air. This is the secondary air per 16 mole S burned. Now calculate the volume of secondary air at 80°F and 735 mm Hg per 100 lb impure sulfur entering (answer to *a*).

On a basis of 100 mole of SO_3-free DCG, calculate the amount of SO_3 absorbed (95% of the amount already calculated for part *a*). Calculate the amount of water necessary to convert the absorbed SO_3 to H_2SO_4. The quantity of 97%w H_2SO_4 which contains this amount of water is the answer to part *b*. Indicate on the diagram the moles of burner gas per 100 lb of impure sulfur and calculate the sensible-heat content for part *c*. Use 80°F as the datum plane. The heat of combustion of sulfur to SO_2 is given at 25°C, which is so close to 80°F that no adjustment need be made.

Solution

a. Volume of secondary air per 100 lb impure sulfur. First find the total sulfur in the DCG.

Basis: 100 mole SO_3-free DCG

$$(88.3 \text{ mole } N_2)\left(\frac{21 \text{ mole } O_2}{79 \text{ mole } N_2}\right) = 23.4 \text{ mole } O_2 \text{ supplied}$$

$$4.2 \text{ mole } O_2 \text{ in } SO_2 + 7.5 \text{ mole } O_2 = 11.7 \text{ mole } O_2 \text{ in DCG}$$

$$23.4 - 11.7 = 11.7 \text{ mole } O_2 \text{ to form } SO_3$$

$$(11.7)\left(\frac{1 \text{ mole } SO_3}{1.5 \text{ mole } O_2}\right) = 7.8 \text{ mole } SO_3 \text{ formed}$$

$$7.8 + 4.2 = 12 \text{ mole S in DCG}$$

Next find secondary air.

Basis: 100 mole SO_3-free DBG. Sixteen mole S enters the converter.

$$(16 \text{ mole S})\left(\frac{88.3 \text{ mole } N_2 \text{ leaving}}{12 \text{ mole S}}\right) = 118 \text{ mole } N_2 \text{ leaving}$$

$$118 - 79 = 39 \text{ mole } N_2 \text{ in, in secondary air}$$

$$(39)(100/79) = 49.4 \text{ mole secondary air}$$

$$(16 \text{ mole S})\left(\frac{32 \text{ lb S}}{\text{mole S}}\right)\left(\frac{100 \text{ lb impure S}}{98 \text{ lb S}}\right) = 523 \text{ lb impure S}$$

$$\left(\frac{49.4 \text{ mole secondary air}}{523 \text{ lb impure S}}\right)(100) = \frac{9.44 \text{ mole secondary air}}{100 \text{ lb impure S}}$$

$$\left[(9.44 \text{ mole})\left(\frac{359 \text{ ft}^3}{\text{mole}}\right)\right]\left(\frac{760}{735}\right)\left(\frac{540}{492}\right) = 3860 \text{ ft}^3 \text{ at } 80° \text{ F and } 735 \text{ mm Hg}$$

b. Pounds of 97% H_2SO_4 per 100 mole SO_3-free DCG

Basis: 100 mole of SO_3-free DCG

$$(7.8 \text{ mole } SO_3)(0.95) = 7.41 \text{ mole } SO_3 \text{ absorbed}$$

$$(7.41 \text{ mole}) \left(\frac{80 \text{ lb } SO_3}{\text{mole } SO_3}\right) = 592 \text{ lb } SO_3 \text{ absorbed}$$

$$(7.41) \left(\frac{18 \text{ lb } H_2O}{\text{mole } SO_3}\right) = 133.3 \text{ lb } H_2O \text{ required}$$

$$(133.3 \text{ lb } H_2O) \left(\frac{100 \text{ lb } 97\% \ H_2SO_4}{3 \text{ lb } H_2O}\right)$$

$$= 4440 \text{ lb } 97\%\text{w } H_2SO_4/100 \text{ mole } SO_3\text{-free DCG}$$

c. Percentage of heat generated in the burner that leaves as sensible heat in the burner gases

Basis: 100 lb impure sulfur

$$(98 \text{ lb S}) \left(\frac{\text{mole S}}{32 \text{ lb S}}\right) = 3.06 \text{ mole S to } SO_2$$

$$(3.06 \text{ mole } SO_2) \left(\frac{100 \text{ mole DBG}}{16 \text{ mole } SO_2}\right) = 19.15 \text{ mole DBG}$$

Therefore, from burner-gas analysis there are 0.96 mole O_2 and 15.13 mole N_2.

Heat generated:

$$(3.06 \text{ mole S to } SO_2) \left(\frac{127{,}690 \text{ Btu}}{\text{mole S to } SO_2}\right) = 391{,}000 \text{ Btu}$$

Sensible heat in gases:

Compound	Mole	Mean C_p between 1300 and 0°F Btu/(mole)(F°)	Btu/F°
SO_2	3.06	11.65	35.7
O_2	0.96	7.66	7.36
N_2	15.13	7.3	110.5
	19.15		153.9

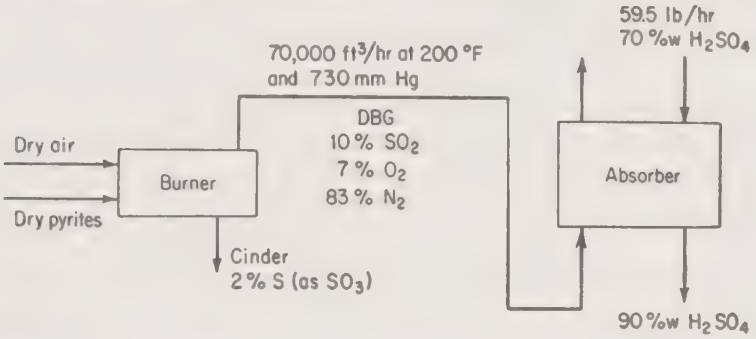
$$\left(\frac{153.9 \text{ Btu}}{\text{F°}}\right) (1300 - 80)\text{F°} = 187{,}800 \text{ Btu}$$

$$\left(\frac{187{,}800}{391{,}000}\right) (100) = 48.07\%$$

Example 6-18. Dry pyrites is burned with dry air in a plant for the manufacture of sulfuric acid by the contact process. The cinder contains 2%w S (present as SO_3).

Seventy thousand cubic feet of burner gas (measured at 730 mm and 200°F) is produced per hour. An analysis of the burner gas shows 10% SO_2 and 7% O_2.

The burner gas is passed through an absorber, where all the SO_3 is removed, and is then conducted to a contact catalyst chamber. Fifty-nine and one-half pounds of 70% H_2SO_4 is used per hour for the absorption of the SO_3 in the burner gas. Ninety per cent H_2SO_4 is formed in the absorber. No SO_3 is formed in the absorber. Calculate the percentage of FeS_2 in the dry pyrites.



Method. On the basis of 1 hr, calculate, by means of a sulfuric acid balance, the moles of SO_3 absorbed. This is all the SO_3 in the 70,000 ft³ of total burner gas. Calculate the moles of burner gas, and subtract the SO_3 quantity to obtain the SO_3-free DBG produced per hour. From the analysis of the burner gas, calculate the moles of SO_3 formed. Subtracting the SO_3 absorbed from the SO_3 formed gives the amount of SO_3 adsorbed on the cinder. Calculate the percentage of SO_3 in the cinder and then the weight of Fe_2O_3 plus gangue produced per hour. Since both the SO_2 and the SO_3 in the burner gas are known, the total sulfur burned, total FeS_2 burned, and total Fe_2O_3 produced per hour can be computed. Subtracting the weight of Fe_2O_3 from the weight of Fe_2O_3 plus gangue gives the amount of gangue associated with the FeS_2 burned. Therefore the percentage of FeS_2 in the dry pyrites can be computed.

Solution

(1) Mole SO_3 absorbed/hr. H_2SO_4 balance (lb). Let Z = mole SO_3 absorbed.

$$(59.5 \text{ lb } 70\% \text{ acid})\left(\frac{0.7 \text{ lb } H_2SO_4}{\text{lb } 70\% \text{ acid}}\right) + (Z \text{ mole } SO_3)\left(\frac{98 \text{ lb } H_2SO_4}{\text{mole } SO_3}\right)$$

$$= \left(\frac{0.9 \text{ lb } H_2SO_4}{\text{lb } 90\% \text{ acid}}\right)(59.5 + 80Z) \text{ lb } 90\% \text{ acid}$$

$$(59.5)(0.7) + Z\,98 = (0.9)(59.5 + Z\,80)$$

$$Z = \frac{0.458 \text{ mole } SO_3 \text{ absorbed}}{\text{hr}}$$

(2) Mole total BG

$$[(70{,}000\ \text{ft}^3)(^{492}/_{660})(^{730}/_{760})](^{1}/_{359}) = 139.4 \text{ mole BG}$$

$$139.4 - 0.5 \text{ mole } SO_3 = 138.9 \text{ mole } SO_3\text{-free DBG}$$

(3) Mole SO_3 in cinder

	SO_3-*free DBG, mole*		*Mole* O_2 *accounted for*
SO_2 (0.10)(138.9)	= (13.89)(11 mole O_2/8 mole S)	=	19.09
O_2 (0.07)(138.9)	= (9.72)(1)	=	9.72
N_2 (0.83)(138.9)	= 115.29		
	138.90		28.81

$$(115.29 \text{ mole } N_2)\left(\frac{21 \text{ mole } O_2}{79 \text{ mole } N_2}\right) = 30.6 \text{ mole } O_2 \text{ supplied}$$

$$-28.8$$

$$1.8 \text{ mole } O_2 \text{ unaccounted for}$$

$$(1.8 \text{ mole } O_2)\left(\frac{8 \text{ mole } SO_3}{15 \text{ mole } O_2}\right) = 0.960 \text{ mole } SO_3 \text{ formed}$$

$$0.960 - 0.458 = 0.502 \text{ mole } SO_3 \text{ in cinder}$$

(4) Amount of FeS_2 and gangue

$$(2 \text{ lb S})\left(\frac{80 \text{ lb } SO_3}{32 \text{ lb S}}\right) = 5\% \ SO_3$$

$$(0.502 \text{ mole } SO_3)\left(\frac{80 \text{ lb}}{\text{mole}}\right)\left(\frac{95 \text{ lb } Fe_2O_3 + \text{gangue}}{5 \text{ lb } SO_3}\right)$$

$$= 761 \text{ lb } Fe_2O_3 + \text{gangue}$$

$$13.89 + 0.96 = 14.85 \text{ mole S burned}$$

$$(14.85)\left(\frac{120 \text{ lb } FeS_2}{2 \text{ mole S}}\right) = 890 \text{ lb } FeS_2$$

$$(890)\left(\frac{160 \text{ lb } Fe_2O_3}{240 \text{ lb } FeS_2}\right) = 594 \text{ lb } Fe_2O_3$$

$$761 - 594 = 167 \text{ lb gangue}$$

$$890 \text{ lb } FeS_2$$

$$1057 \text{ lb pyrites}$$

$$(^{890}/_{1057})(100) = 84.4\% \ FeS_2$$

Example 6-19. A sulfuric acid plant burns pyrites containing 85.3% FeS_2, 2% H_2O, and 12.7% gangue. The air used is moisture-free. Both the air and the pyrites are supplied at 75°F. At 25°C a poundmole of FeS_2 releases either 371,000 Btu in burning to SO_2 or 422,000 Btu in burning to SO_3. The cinder contains 0.42% S as FeS_2 and leaves the burner at 900°F. The heat capacity of the cinder is 0.18 Btu/(lb)(F°).

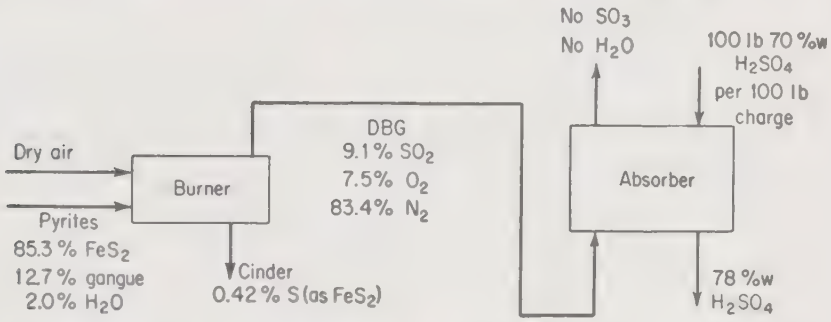
The burner-gas analysis is 9.1% SO_2, 7.5% O_2, and 83.4% N_2, and the gas is at 1000°F. All the SO_3 formed in the burner is carried into an absorption tower along with the burner gas. This tower is fed with 100 lb 70% H_2SO_4/100 lb pyrites fired. Part of the SO_2 in the burner gas is converted to SO_3 and then into H_2SO_4 in this tower, and the acid stream leaving the tower contains 78% H_2SO_4. The exit gas from the tower contains no SO_3 and is also moisture-free. Calculate the following:

a. The pounds of FeS_2 lost in the cinder, per 100 lb pyrites fed to the plant

b. The moles of SO_3 in the burner gas per 100 lb pyrites fed

c. The percentage of the SO_2 in the burner gas that is converted to SO_3 in the absorption tower

d. The heat dissipated from the burner, per 100 lb pyrites fired



Method. On the basis of 100 lb of pyrites, let the amount of FeS_2 in the cinder be represented by z. The sulfur in z lb of pyrites is the sulfur in the cinder. The amount of gangue is known, and the amount of Fe_2O_3 formed can be expressed in terms of z. Write a sulfur balance, equating the sulfur in the pyrites lost (an expression in terms of z) to 0.42% of the weight of the cinder (another expression in terms of z). Solve for z, the answer to part *a*. Now calculate the mole S fired, mole S lost, and mole S gasified. On the basis of 100 mole SO_3-free DBG, calculate from the gas analysis the mole SO_3 formed and total mole S in the DBG. From the mole S gasified/100 lb pyrites and mole SO_3/mole S in the DBG (this is sulfur gasified) compute the mole SO_3 in DBG/100 lb of pyrites (answer to *b*). On the basis of 100 lb of pyrites, calculate by a sulfuric acid balance the total SO_3 absorbed. Subtracting answer *b* from this quantity gives the mole SO_3 made in the absorber. Subtracting answer *b* from mole S gasified gives mole S as SO_2 in DBG. Therefore the percentage of the SO_2 in the burner gas that is converted to SO_3 in the absorption tower may be computed. This is answer *c*. Indicate on the diagram the weight of the cinder and the moles of burner gas per 100 lb pyrites. Calculate the heat generated, sensible heat in the cinder,

and sensible and latent heat in the burner gases. Determine the heat dissipated by subtraction.

Solution

a. FeS_2 lost in cinder/100 lb pyrites

Basis: 100 lb pyrites. Let z = lb FeS_2 in cinder.

$$85.3 - z = \text{lb } FeS_2 \text{ burned}$$

$$(z \text{ lb } FeS_2 \text{ lost})\left(\frac{64 \text{ lb S}}{120 \text{ lb } FeS_2}\right) = (0.0042)\left[(85.3 - z)\left(\frac{160 \text{ lb } Fe_2O_3}{240 \text{ lb } FeS_2}\right) + 12.7 + z\right]$$

$$z = 0.549 \text{ lb } FeS_2$$

b. Mole SO_3 in DBG/100 lb pyrites

Basis: 100 lb pyrites

$$(85.3 \text{ lb } FeS_2)\left(\frac{2 \text{ mole S}}{120 \text{ lb } FeS_2}\right) = 1.421 \text{ mole S fired}$$

$$(0.549 \text{ lb } FeS_2)\left(\frac{2}{120}\right) = \frac{0.009 \text{ mole S lost}}{1.412 \text{ mole S gasified}}$$

Basis: 100 mole SO_3-free DBG

$$(83.4 \text{ } N_2)(\tfrac{21}{79}) = 22.2 \text{ mole } O_2 \text{ supplied}$$

$$(9.1 \text{ mole } SO_2)\left(\frac{11 \text{ mole } O_2}{8 \text{ mole } SO_2}\right) = 12.5 + 7.5 \text{ mole } O_2$$

$$= 20.0 \text{ mole } O_2 \text{ accounted for}$$

$$22.2 - 20.0 = (2.20 \text{ mole } O_2)(\text{to } SO_3)\left(\frac{8 \text{ mole } SO_3}{15 \text{ mole } O_2}\right)$$

$$= 1.175 \text{ mole } SO_3$$

$$9.1 \text{ mole S in } SO_2 + 1.175 \text{ mole S in } SO_3 = 10.27 \text{ mole S in DBG}$$

$$(1.412 \text{ mole S gasified})\left(\frac{1.175 \text{ mole } SO_3}{10.27 \text{ mole S gasified}}\right)$$

$$= \frac{0.1616 \text{ mole } SO_3 \text{ in DBG}}{100 \text{ lb pyrites}}$$

c. Percentage of SO_2 in the DBG converted to SO_3 in the absorber

Basis: 100 lb pyrites. 100 lb 70%w H_2SO_4 supplied. Let z = mole SO_3 absorbed.

H_2SO_4 balance (lb):

$$70 + 98z = (0.78)(100 + 80z)$$

$$z = 0.225 \text{ mole } SO_3 \text{ absorbed}$$

$$0.225 - 0.1616 = 0.0634 \text{ mole } SO_3 \text{ made in absorber}$$

$$1.412 \text{ mole S gasified} - 0.1616 \text{ mole } SO_3 = 1.250 \text{ mole } SO_2 \text{ in DBG}$$

Therefore,

$$\left(\frac{0.0634}{1.250}\right)(100) = 5.07\%$$

d. Heat dissipated from the burner per 100 lb pyrites fired

Weight of cinder:

$$(85.3 - 0.549)\text{ lb } FeS_2 \left(\frac{160\text{ lb } Fe_2O_3}{240\text{ lb } FeS_2}\right) = 56.5\text{ lb } Fe_2O_3 \text{ formed}$$

$$56.5\text{ lb } Fe_2O_3 + 0.549\text{ lb } FeS_2 + 12.7\text{ lb gangue} = 69.8\text{ lb cinder}$$

Mole of burner gases:

$$(1.412\text{ mole S gasified}) \left(\frac{100\text{ mole } SO_3\text{-free DBG}}{10.27\text{ mole S}}\right) = 13.76\text{ mole } SO_3\text{-free DBG}$$

$$(13.76) \left(\frac{0.091\text{ mole } SO_2}{\text{mole } SO_3\text{-free DBG}}\right) = 1.25\text{ mole } SO_2$$

$$(13.76)(0.075) = 1.03\text{ mole } O_2$$

$$(13.76)(83.4) = \frac{11.48\text{ mole } N_2}{13.76}$$

Heat generated in the burner. Take 75°F as the datum temperature.

$$(1.25\text{ mole } SO_2) \left(\frac{1\text{ mole } FeS_2}{2\text{ mole } SO_2}\right) \left(\frac{371{,}000\text{ Btu}}{\text{mole } FeS_2}\right) = 232{,}000\text{ Btu}$$

$$(0.1616\text{ mole } SO_3) \left(\frac{1\text{ mole } FeS_2}{2\text{ mole } SO_3}\right) \left(\frac{422{,}000\text{ Btu}}{\text{mole } FeS_2}\right) = 34{,}100\text{ Btu}$$

$$232{,}000 + 34{,}100 = 266{,}100\text{ Btu}$$

Heat in cinder:

$$(69.8\text{ lb cinder}) \left(\frac{0.18\text{ Btu}}{\text{mole F°}}\right) (900 - 75)\text{ F°} = 10{,}360\text{ Btu}$$

Heat in gases:

Sensible:

Compound	Mole	Mean C_p between 1000°F and 0°F in Btu/(mole)(F°)	Btu/F°
SO_3	0.1616	12.00	1.939
SO_2	1.250	11.2	14.00
O_2	1.030	7.51	7.74
N_2	11.48	7.15	82.1
H_2O	0.1111	8.54	0.949
			106.7

$$\left(\frac{106.7\text{ Btu}}{\text{F°}}\right) (1000 - 75)\text{F°} = 98{,}700\text{ Btu}$$

Latent:

$$(2\text{ lb } H_2O) \left(\frac{1060\text{ Btu}}{\text{lb}}\right) = 2120\text{ Btu}$$

$$266{,}100 - 10{,}360 - 98{,}700 - 2120 = 154{,}920\text{ Btu}$$

VINYL ACETATE MANUFACTURE

Let us pretend that you work for a large chemical company, in the process design department. Let us say further that you are concerned with organic chemicals. For many years your company has been developing chemical processes through its own research establishment. In the normal course of such work, you are asked to evaluate a process at each level of its development. This means to estimate the selling price of the product. When a process is little more than a gleam in a chemist's eye, you make many assumptions (for example, about the yields and conversions that will be obtainable on the industrial scale) and use simplified calculation methods (for example, to determine the size of a distillation column) and generalized cost-estimation methods. If the process looks economically promising, it then passes through further experimental stages in which progressively larger quantities are produced, and evaluations at these stages are used to keep management informed of the economic potential at all times. Since more facts are being obtained about the process during these successive experimental stages, fewer assumptions have to be made in the successive economic evaluations. If the company eventually decides to build a plant, your department does a full-fledged plant design. This involves use of the most rigorous calculation methods and solicitation of bids from contractors and equipment manufacturers. At this stage, other engineers are working with you on the design. For example, mechanical engineers may be designing foundations and certain equipment, and instrumentation-department people may be planning for the control of the operation by instruments which are sensitive to temperature, pressure, and other process stimuli. The total development of the process from laboratory to final plant usually takes several years.

Now let us suppose that the company has become interested in the manufacture of vinyl acetate monomer. This may be made through the reaction of acetylene with acetic acid as indicated by the equation

$$C_2H_2 \text{ (acetylene)} + CH_3COOH \text{ (acetic acid)} \rightarrow CH_3COOCHCH_2 \text{ (vinyl acetate)}$$

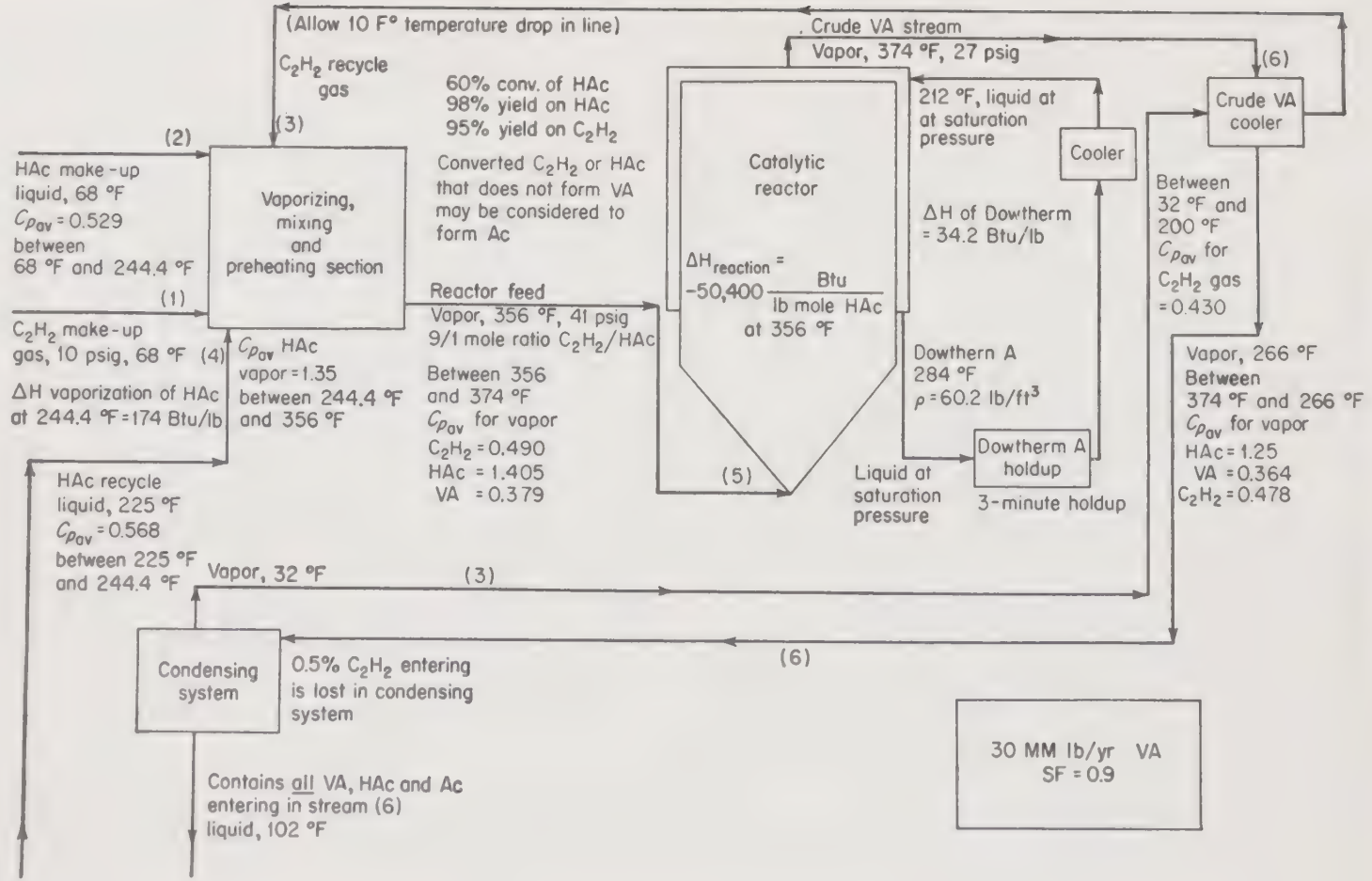
It was manufactured in Germany by the Wacker process in which the reaction was carried out in the vapor phase over a zinc acetate catalyst. The catalyst was made by precipitating zinc acetate on pellets of activated carbon which were a few millimeters in diameter. A vessel was filled with these pellets, and the reactants were blown through at an appropriate temperature and pressure. Several such vessels were required because the catalyst activity diminished with use. After World

War II German patents were made available by the U.S. government. These in essence are "spoils of war" and part of the public domain. Your research organization had an idea that the process would be more efficient if the reaction were run in "fluidized-bed" reactors. These reactors are designed in such a way that the vapor flowing through lifts and thoroughly agitates the small catalyst pellets. The entire "bed" of particles expands as the vapor is admitted until, at the design velocity of vapor, the "bed" has a fluid appearance and will flow like a fluid. This fluidization is beneficial in two ways. In the first place, it provides intimate contact between the vapor and the catalyst and ensures uniform temperature distribution throughout the bed. In the second place, since the solids will flow, it becomes possible to withdraw a constant percentage of the catalyst and add a like quantity of fresh catalyst which will mix thoroughly and maintain the bed at constant catalyst-activity level. The process may therefore be run continuously, with the reactor discharging an effluent of constant composition which may be processed continuously in the necessary equipment. Early experimental work by the research staff has shown promising results. You are asked to make an economic evaluation based on the laboratory data.

It is now necessary for you to draw a "flow diagram" indicating the processing equipment that will be necessary in an industrial plant, and the order of processing. You will also decide, probably with the aid of a market-development group, the yearly production of the plant and its location. Then you will make a complete material balance and complete heat balance on the process, calculate the sizes of the pieces of equipment, decide what materials of construction must be used, and estimate the capital cost of the equipment. Next you will estimate the size and cost of utilities and off-site facilities (steam plant, electrical distribution system, cooling-water system, docks, storehouses, change houses, shops, roads, sewers, administration building, etc.). Finally you will estimate a cost of manufacture of the vinyl acetate, using economic factors which include the daily cost of utilities consumed, wages, material and overhead for the operating and maintenance personnel, taxes, insurance and land rental, and equipment amortization at a rate which your company deems attractive. We are going to examine a typical material balance and selected parts of the heat balance in an attempt to reveal the role of stoichiometry in this work.

Following is a schematic diagram of the process, arranged in such a manner that we may concentrate on the material balance and certain segments of the heat balance. A description of the process, questions, and the solution follow.

Description of the Process and Design Considerations. Make-up and recycle acetic acid (hereafter HAc) is vaporized and mixed with


(Allow 10 F° temperature drop in line)
C_2H_2 recycle gas
(3)
(2)
HAc make-up liquid, 68 °F
$C_{p_{av}}$ = 0.529 between 68 °F and 244.4 °F
(1)
C_2H_2 make-up gas, 10 psig, 68 °F (4)
ΔH vaporization of HAc at 244.4 °F = 174 Btu/lb
Vaporizing, mixing and preheating section
$C_{p_{av}}$ HAc vapor = 1.35 between 244.4 °F and 356 °F
60% conv. of HAc
98% yield on HAc
95% yield on C_2H_2
Converted C_2H_2 or HAc that does not form VA may be considered to form Ac
Reactor feed
Vapor, 356 °F, 41 psig
9/1 mole ratio C_2H_2/HAc
Between 356 and 374 °F
$C_{p_{av}}$ for vapor
C_2H_2 = 0.490
HAc = 1.405
VA = 0.379
Catalytic reactor
$\Delta H_{reaction} = -50{,}400 \frac{Btu}{lb\ mole\ HAc}$ at 356 °F
(5)
. Crude VA stream
Vapor, 374 °F, 27 psig
212 °F, liquid at at saturation pressure
Cooler
ΔH of Dowtherm = 34.2 Btu/lb
Dowtherm A
284 °F
ρ = 60.2 lb/ft^3
Dowtherm A holdup
3-minute holdup
Liquid at saturation pressure
(6)
Crude VA cooler
Between 32 °F and 200 °F
$C_{p_{av}}$ for C_2H_2 gas = 0.430
Vapor, 266 °F
Between 374 °F and 266 °F
$C_{p_{av}}$ for vapor
HAc = 1.25
VA = 0.364
C_2H_2 = 0.478
HAc recycle liquid, 225 °F
$C_{p_{av}}$ = 0.568 between 225 °F and 244.4 °F
Vapor, 32 °F
(3)
(6)
Condensing system
0.5% C_2H_2 entering is lost in condensing system
Contains all VA, HAc and Ac entering in stream (6) liquid, 102 °F
30 MM lb/yr VA
SF = 0.9

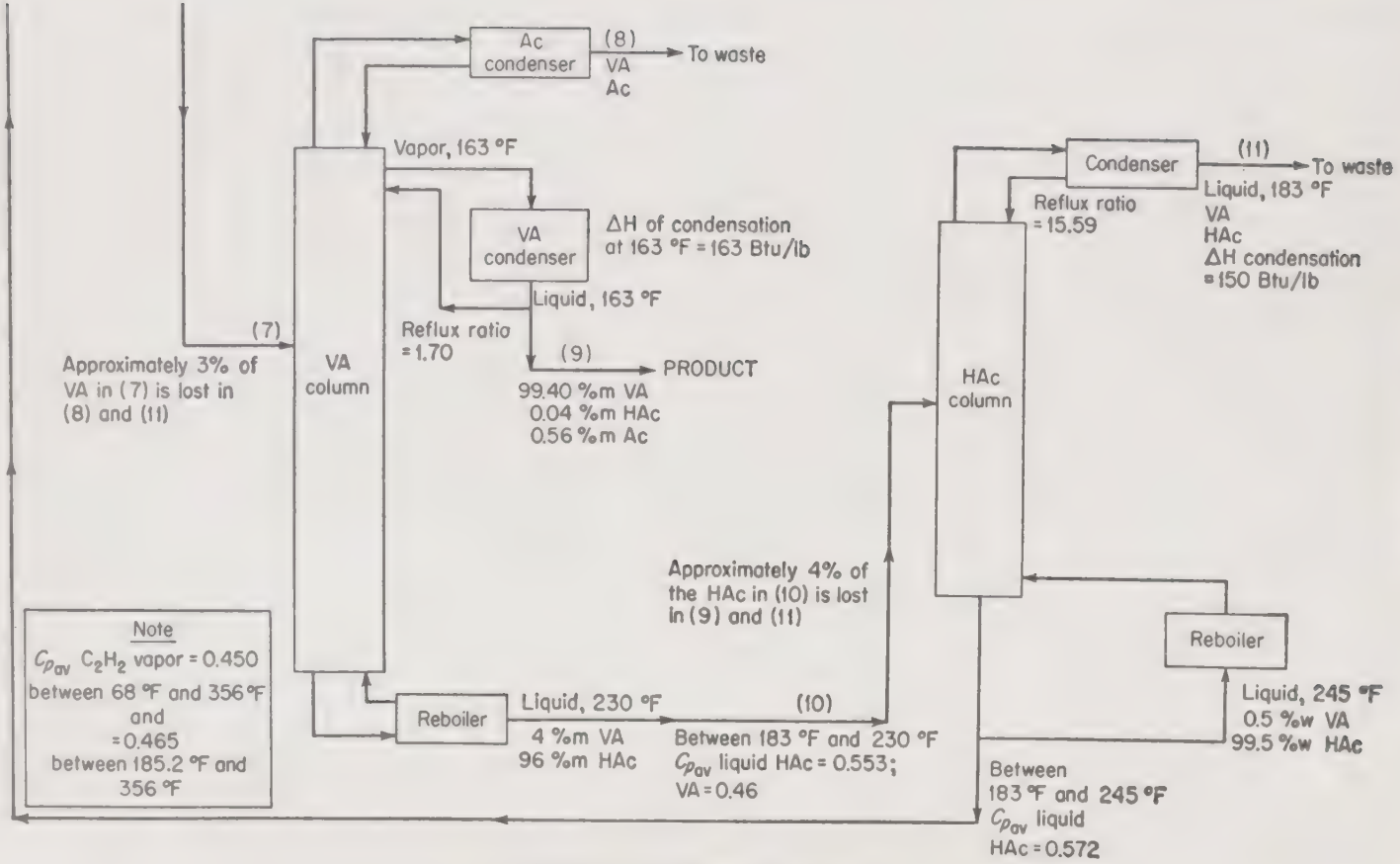


FIG. 6-2. Vinyl acetate process.

make-up and recycle acetylene (C_2H_2) and preheated to 356°F in the first section of the plant. For simplicity, we shall not deal with the individual pieces of equipment that effect the vaporizing, mixing, and preheating. We shall assume for our material balance that the make-ups HAc and C_2H_2 are pure because we believe that the small amount of impurities which they do contain will pass off with impurities formed in the reactor and therefore will neither require any extra processing equipment nor build up to such a level in recycle streams that they would affect equipment size

The gaseous mixture is blown through the catalytic reactor where 60% of the HAc is converted with a 98% yield to vinyl acetate (VA). The yield of VA on C_2H_2 is 95%. These data plus the temperatures and pressures are based on actual experimental runs on a bench scale. Laboratory information also enables us to decide that we shall treat all the impurities formed as acetaldehyde (CH_3COH, hereafter Ac) since it is the major impurity and the minor ones would go along with it in the processing. The hot gaseous effluent from the reactor therefore contains unreacted C_2H_2 and HAc, VA, and Ac. For our material balance we shall not show the catalyst preparation, storage, make-up, and withdrawal streams. The crude VA effluent proceeds through a cooler to a condensation system. We shall not examine the individual heat exchangers in this system, but our judgment is that a small loss of C_2H_2 will occur and an essentially complete separation of C_2H_2 from the other compounds will be effected. The cool acetylene is recycled through the crude VA cooler. The condensate in stream 7 passes to a distillation column in which Ac is taken off overhead and the final product, VA, is a side stream. The bottoms from the VA column are distilled in a second column where VA is removed overhead. We believe that the recycle HAc should not contain much VA since its presence tends to lower the yield in the reactor. In keeping with plant experience, we decide to expect a 3% (approximately) loss of VA in the columns and a 4% (approximately) loss of HAc. We know the composition of the desired product, and we choose the other compositions and temperatures given on the diagram on the basis of distillation economy consistent with product purity, material losses, and recycle-stream composition.

Example 6-20. Using the information in the diagram, calculate the following:

a. A material balance, showing amounts of each constituent in the numbered streams

b. Quantity of heat in Btu/SH that must be added in the vaporizing, mixing, and preheating sections

c. Size (in gallons) of the holdup tank for the Dowtherm A

d. Quantity of heat in Btu/SH that must be removed in the VA condenser

e. Quantity of heat in Btu/SH that must be added in the reboiler of the HAc column

Note the use of the term Btu/SH. The on-stream factor (SF) is 0.9, as indicated in the diagram. This means that we are assuming that the plant will be operated (around the clock) for nine-tenths of the year. We are allowing one-tenth of the time for unscheduled shutdowns. We shall therefore design the equipment to process, in one on-stream hour, 1/0.9 times as much material as it would process if it could be depended upon to run with no shutdowns.

Solution

a. Material balance.

Basis: 100 mole of VA formed in the reactor*

Calculation of compositions of streams 4, 5, and 6:

$$(100 \text{ mole VA formed}) \left(\frac{1 \text{ mole HAc to VA}}{\text{mole VA}}\right) \left(\frac{0.02 \text{ mole HAc to Ac}}{0.98 \text{ mole HAc to VA}}\right)$$
$$= 2.04 \text{ mole HAc to Ac}$$

$$100 + 2.04 = 102.04 \text{ mole HAc reacting}$$

$$(102.04 \text{ mole HAc reacting}) \left(\frac{0.40 \text{ mole HAc unconverted}}{0.60 \text{ mole HAc reacting}}\right)$$
$$= 68.1 \text{ mole HAc in stream 6}$$

$$102.04 + 68.1 = 170.14 \text{ mole HAc in stream 5}$$

$$(170.14 \text{ mole HAc}) \left(\frac{9 \text{ mole } C_2H_2}{\text{mole HAc}}\right) = 1531.26 \text{ mole } C_2H_2 \text{ in stream 5}$$

$$(100 \text{ mole VA formed}) \left(\frac{1 \text{ mole } C_2H_2 \text{ to VA}}{\text{mole VA}}\right) \left(\frac{0.05 \text{ mole } C_2H_2 \text{ to Ac}}{0.95 \text{ mole } C_2H_2 \text{ to VA}}\right)$$
$$= 5.27 \text{ mole } C_2H_2 \text{ to Ac}$$

$$100 + 5.27 = 105.27 \text{ mole } C_2H_2 \text{ reacting}$$

$$1531.26 - 105.27 = 1425.99 \text{ mole } C_2H_2 \text{ in stream 6}$$

* *Note:* This type of calculation usually requires the use of a desk calculating machine to maintain "significant figures." Since we are restricted to the use of the slide rule, we shall try to do the calculations in such a way as to get the best accuracy. For example, if, in the reaction $A + B \rightarrow C$, 99.5% of the A that is present reacts and 100 mole of C is formed, and we want to determine how much A is left unreacted, we might write

$$(100 \text{ mole } C \text{ formed}) \left(\frac{1 \text{ mole } A \text{ reacts}}{1 \text{ mole } C \text{ formed}}\right) \left(\frac{0.5 \text{ mole } A \text{ unreacted}}{99.5 \text{ mole } A \text{ reacted}}\right)$$
$$= 0.503 \text{ mole } A \text{ unreacted}$$

rather than

$$(1 \text{ mole } C \text{ formed}) \left(\frac{1 \text{ mole } A \text{ reacts}}{1 \text{ mole } C \text{ formed}}\right) \left(\frac{1 \text{ mole } A \text{ originally present}}{0.995 \text{ mole } A \text{ reacting}}\right)$$
$$= 100.5 \text{ mole } A \text{ originally present}$$

$$100.5 - 100 = 0.5 \text{ mole } A \text{ unreacted}$$

$$(2.04 \text{ mole HAc to Ac})\left(\frac{60.1 \text{ lb HAc}}{\text{mole HAc}}\right) = 122.5 \text{ lb Ac formed}$$

$$(5.27 \text{ mole } C_2H_2 \text{ to Ac})\left(\frac{26 \text{ lb Ac}}{\text{mole Ac}}\right) = 136.8$$

$$259.3 \text{ lb formed}$$

$$(259.3 \text{ lb Ac})\left(\frac{\text{mole Ac}}{44.1 \text{ lb Ac}}\right) = 5.88 \text{ mole Ac in stream 6}$$

The amount of VA leaving will be 100 mole plus the moles of VA entering. The moles of VA entering depends on the amount of recycle HAc. Examination of the diagram indicates that the percentage of HAc in the product is very small. Therefore if we assume that all the HAc in the reactor effluent leaves the VA column in stream 10 and that 96% of this HAc is in the recycle stream we shall be in error by an amount so small that it is unlikely to upset our requirement of 4% loss of HAc. If there were an appreciable quantity of HAc in the product, we could not simplify the calculation in this way. The recycle stream contains

$$\left(\frac{0.5 \text{ lb VA}}{99.5 \text{ lb HAc}}\right)\left(\frac{\text{mole VA}}{86.1 \text{ lb VA}}\right)\left(\frac{60.1 \text{ lb HAc}}{\text{mole HAc}}\right) = 0.00351 \frac{\text{mole VA}}{\text{mole HAc}}$$

$$(68.1 \text{ mole HAc in stream 7})\left(\frac{0.04 \text{ mole HAc lost}}{\text{mole HAc processed}}\right)$$

$$= 2.72 \text{ mole HAc lost}$$

$$68.1 - 2.72 = 65.38 \text{ mole HAc in stream 4}$$

$$(65.38 \text{ mole HAc})\left(\frac{0.00351 \text{ mole VA}}{\text{mole HAc}}\right) = 0.229 \text{ mole VA in stream 4}$$

$$100 + 0.229 = 100.229 \text{ mole VA in stream 6}$$

Stream 4 contains 65.38 mole HAc and 0.229 mole VA.

Stream 5 contains 1531.26 mole C_2H_2, 170.14 mole HAc, and 0.229 mole VA.

Stream 6 contains 1425.99 mole C_2H_2, 68.1 mole HAc, 100.229 mole VA, and 5.88 mole Ac.

Calculation of compositions of streams 1, 2, 3, and 7:

Since the HAc in stream 5 comes from 4 and 2, stream 2 contains

$$170.14 - 65.38 = 104.76 \text{ mole HAc}$$

(This equals the 102.04 mole that react plus the 4% of the unreacted 68.1 mole that is lost.)

0.5% of the C_2H_2 in stream 6 is lost.

$$1425.99(0.005) = 7.13 \text{ mole lost}$$

Stream 3 contains $1425.99 - 7.13 = 1418.86$ mole C_2H_2.
Stream 7 contains 100.229 mole VA, 68.1 mole HAc_1 and 5.88 mole Ac.
Since the C_2H_2 in stream 5 comes from 3 and 1, stream 1 contains

$$1531.26 - 1418.86 = 112.40 \text{ mole } C_2H_2$$
(105.27 mole react and 7.13 mole are lost.)

Calculation of composition of streams 8, 9, 10, and 11:

To make the material balance on the distillation section we note again that the total quantity of HAc in the product is negligible. Therefore the HAc in stream 7 is in stream 10 and 96% of it is in 4 accompanied by 0.229 mole VA as previously calculated.

Three per cent of the VA in stream 7 is lost in 8 and 11.

$$(100.229 \text{ mole VA})(0.03) = 3.01 \text{ mole VA lost}$$

Stream 9 must contain $100.229 - 3.01 - 0.229 = 96.99$ mole VA

$$\text{plus} \quad (96.99 \text{ mole VA}) \left(\frac{0.04 \text{ mole HAc}}{99.4 \text{ mole VA}} \right) = 0.0390 \text{ mole HAc}$$

$$\text{plus} \quad (96.99) \left(\frac{0.56 \text{ mole Ac}}{99.4 \text{ mole VA}} \right) = 0.546 \text{ mole Ac}$$

Stream 10 contains $68.10 - 0.0390 = 68.06$ mole HAc

$$\text{plus} \quad (68.06 \text{ mole HAc}) \left(\frac{0.04 \text{ mole VA}}{0.96 \text{ mole HAc}} \right) = 2.84 \text{ mole VA}$$

Stream 8 contains $100.229 - 96.99 - 2.84 = 0.40$ mole VA

$$\text{plus} \quad 5.88 - 0.546 = 5.33 \text{ mole Ac}$$

Stream 11 contains $68.06 - 65.38 = 2.68$ mole HAc

$$\text{plus} \quad (3.01)(\text{mole VA lost}) - 0.40 (\text{mole lost in stream 8}) = 2.61 \text{ mole VA}$$

MATERIAL BALANCE, MOLE

Compound	(1)	(2)	(3)	(4)	(5)	In reactor	(6)	(7)	Loss of C_2H_2	(8)	(9)	(10)	(11)
C_2H_2	112.40	.....	1418.86	.....	1531.26	−105.27	1425.99	.....	−7.13				
VA	.....	.....	.....	0.229	0.229	+100	100.229	100.229	.....	0.40	96.99	2.84	2.61
HAc	.....	104.76	.....	65.38	170.14	−102.04	68.10	68.10	.....	....	0.0390	68.06	2.68
Ac	.....	.....	.....	.....	.....	+5.88	5.88	5.88	.....	5.33	0.546		

In the following, CY = calendar year, SY = stream year, etc.

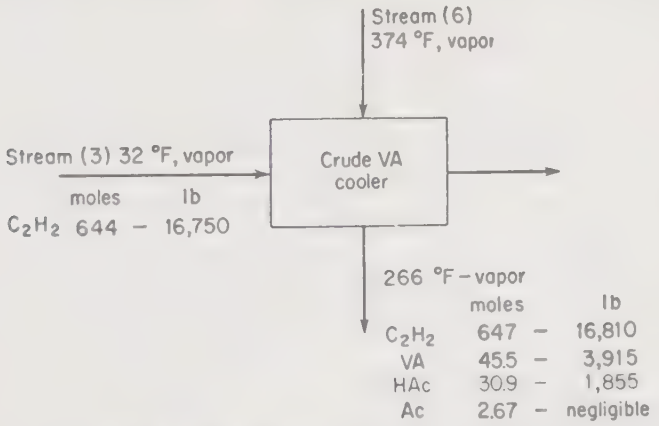
$$\left(\frac{30 \text{ MM lb VA}}{\text{CY}}\right)\left(\frac{\text{CY}}{0.9 \text{ SY}}\right)\left(\frac{\text{SY}}{365 \text{ SD}}\right)\left(\frac{\text{SD}}{24 \text{ SH}}\right)\left(\frac{\text{mole VA}}{86.1 \text{ lb VA}}\right) = \frac{44.0 \text{ mole VA}}{\text{SH}}$$

Since the material balance shows 96.99 mole VA, we shall reduce it by the factor 44.0/96.99 = 0.454.

ANSWER TO *a*. FINAL MATERIAL BALANCE, MOLE
Basis: One Stream Hour

Compound	(1)	(2)	(3)	(4)	(5)	In reactor	(6)	(7)	Loss of C_2H_2	(8)	(9)	(10)	(11)
C_2H_2	51.0		644		695	−47.8	647		−3.24				
VA				0.104	0.104	+45.4	45.5	45.5		0.182	44.0	1.290	1.185
HAc		47.5		29.7	77.2	−46.3	30 9	30.9			0.018	30.9	1.217
Ac						+2.67	2.67	2.67		2.42	0.248		

b. Heat added in vaporizing, mixing, and preheating section. First we calculate the temperature of stream 3 when it leaves the crude VA cooler.



$$q = \left(m \frac{\text{lb}}{\text{SH}}\right)\left(\frac{C_p \text{ Btu}}{(\text{lb})(\text{F}^\circ)}\right)(\text{F}^\circ \text{ temperature rise})$$

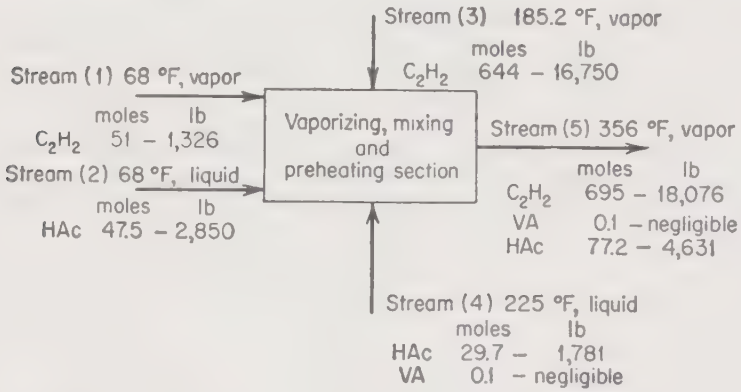
$$q_{\text{HAc}} = (1855)(1.25)(374 - 266) = 250{,}500 \text{ Btu/SH}$$
$$q_{\text{VA}} = (3915)(0.364)(374 - 266) = 153{,}800$$
$$q_{C_2H_2} = (16{,}810)(0.478)(374 - 266) = 770{,}000$$
$$1{,}174{,}300 \text{ Btu/SH}$$

Finding the exit temperature of C_2H_2 is a trial-and-error procedure. The exit temperature is assumed, average C_p calculated, and exit temperature calculated until agreement is obtained. In the diagram it is suggested that $C_p = 0.430$ (exit temperature of 200°F) be tried. In a calculation of this type you would, of course, need a table of heat capacities of acetylene. In the absence of this we have taken the liberty of giving the correct trial value. Since $q = mC_{p_{av}}\,\Delta t$ and since all the heat taken from stream 6 goes to stream 3,

$$1{,}174{,}300 = (16{,}750)(0.430)\,\Delta t$$
$$\Delta t = 163.2\ \text{F°}$$
$$\text{Exit } t = 163.2 + 32 = 195.2\text{°F}$$

This agrees sufficiently well with 200°F since a change of 5 degrees in a new assumed value would not change $C_{p_{av}}$.

We may now write the heat balance around the mixing section.



Heat for stream 1:

$$\left(\frac{1326\ \text{lb}}{\text{SH}}\right)\left(\frac{0.450\ \text{Btu}}{(\text{lb})(\text{F°})}\right)(356 - 68)\ \text{F°} = \frac{172{,}000\ \text{Btu}}{\text{SH}}$$

Heat for stream 3:

$$\left(\frac{16{,}750\ \text{lb}}{\text{SH}}\right)\left(\frac{0.465\ \text{Btu}}{(\text{lb})(\text{F°})}\right)(356 - 185.2) = \frac{1{,}330{,}000\ \text{Btu}}{\text{SH}}$$

Heat for stream 2 to raise liquid to boiling point, 244.4°F:

$$\left(\frac{2850\ \text{lb}}{\text{SH}}\right)(0.529)(244.4 - 68) = \frac{266{,}000\ \text{Btu}}{\text{SH}}$$

Heat for stream 4 to raise liquid to boiling point of HAc, 244.4°F:

$$\left(\frac{1781 \text{ lb}}{\text{SH}}\right)(0.568)(244.4 - 225) = \frac{19{,}680 \text{ Btu}}{\text{SH}}$$

Heat to vaporize streams 2 and 4:

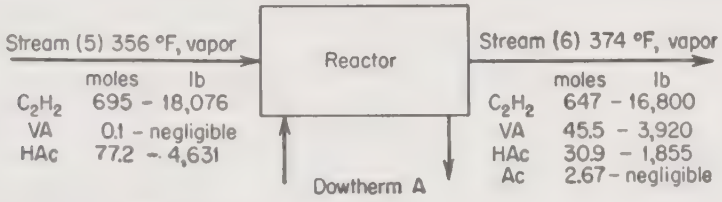
$$\left(\frac{4631 \text{ lb}}{\text{SH}}\right)\left(\frac{174 \text{ Btu}}{\text{lb}}\right) = \frac{808{,}000 \text{ Btu}}{\text{SH}}$$

Heat to raise HAc vapor from 244.4 to 356°F:

$$\left(\frac{4631 \text{ lb}}{\text{SH}}\right)(1.35)(356 - 244.4) = 699{,}000 \frac{\text{Btu}}{\text{SH}}$$

$$172{,}000 + 1{,}330{,}000 + 266{,}000 + 19{,}680 + 808{,}000 + 699{,}000 = \frac{3{,}295{,}000 \text{ Btu}}{\text{SH}}$$

c. Capacity of holdup tank. First we must find the heat removed by Dowtherm A.



Heat of reaction liberated:

$$\left(\frac{45.5 \text{ mole VA}}{\text{SH}}\right)\left(\frac{50{,}400 \text{ Btu}}{\text{mole}}\right) = \frac{2{,}200{,}000 \text{ Btu}}{\text{SH}}$$

Heat absorbed by major constituents:

$$q_{C_2H_2} = (16{,}800)(0.490)(374 - 356) = \frac{147{,}000 \text{ Btu}}{\text{SH}}$$

$$q_{HAc} = (1855)(1.045)(374 - 356) = \frac{34{,}900 \text{ Btu}}{\text{SH}}$$

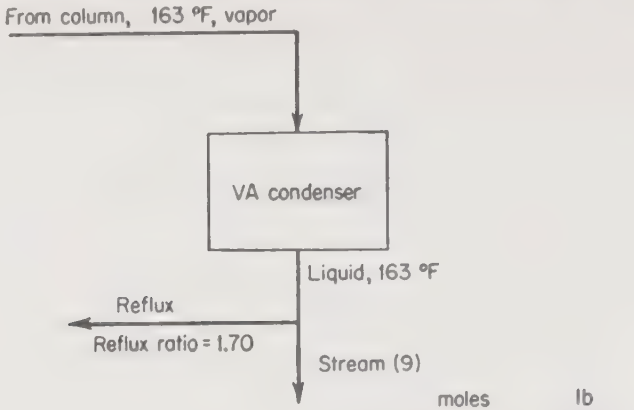
$$q_{VA} = (3920)(0.379)(374 - 356) = \frac{27{,}200 \text{ Btu}}{\text{SH}}$$

$$2{,}200{,}000 - 147{,}000 - 34{,}900 - 27{,}200 = \frac{1{,}991{,}000 \text{ Btu}}{\text{SH}}$$

$$\left(\frac{1{,}991{,}000 \text{ Btu absorbed by Dowtherm A}}{\text{SH}}\right)\left(\frac{\text{lb}}{34.2 \text{ Btu}}\right) = \frac{58{,}300 \text{ lb}}{\text{SH}}$$

$$\left(\frac{58{,}300 \text{ lb}}{\text{SH}}\right)\left(\frac{\text{ft}^3}{60.2 \text{ lb}}\right)\left(\frac{\text{SH}}{60 \text{ SM}}\right)\left(\frac{7.48 \text{ gal}}{\text{ft}^3}\right)(3 \text{ min holdup}) = 363 \text{ gal}$$

d. Heat removed by VA condenser. There are (44.0)(1.70) = 74.6

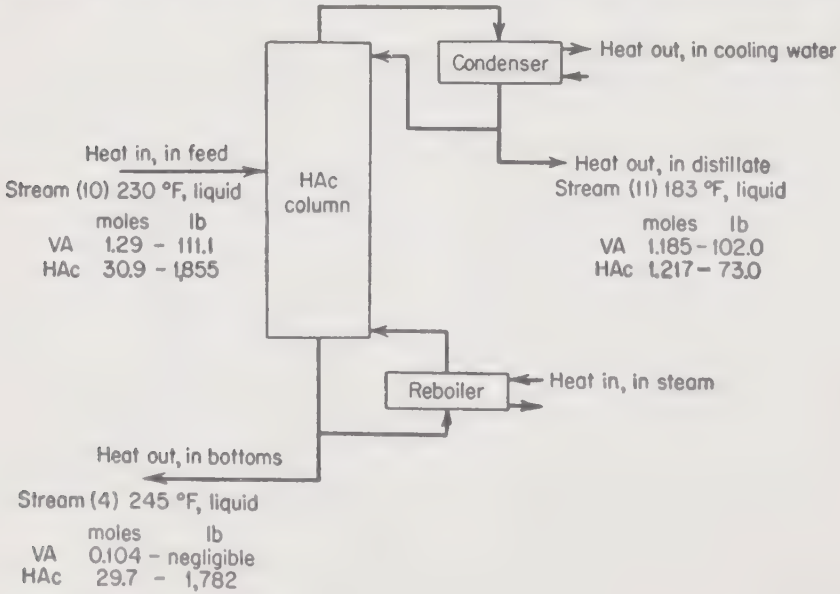


mole VA in the reflux stream and 44.0 + 74.6 = 118.6 mole VA in the stream to the condenser.

$$(118.6 \text{ mole VA})\left(\frac{86.1 \text{ lb VA}}{\text{mole VA}}\right) = \frac{10{,}200 \text{ lb to be condensed}}{\text{SH}}$$

$$(10{,}200)(163) = \frac{1{,}662{,}000 \text{ Btu to be removed}}{\text{SH}}$$

e. Heat to be added in the HAc reboiler. This may be determined by an over-all heat balance on the HAc column. The composition of the



distillate is

$$\left(\frac{1.185}{1.185 + 1.217}\right)(100) = 49.4\%\text{m VA}$$

The boiling point of this stream is 183°F. This would have to be determined from a boiling-point curve for the VA-HAc system. Since this is not included in the text, the temperature is given on the diagram. Note that it would *not* be known until *after* the material balance had been made.

Take 183°F, liquid state, as the datum.

Heat in, in feed above 183°F:

$$q_{HAc} = (1855)(0.553)(230 - 183) = 48{,}200$$
$$q_{VA} = (111.1)(0.46)(230 - 183) = \underline{2{,}400}$$
$$50{,}600 \text{ Btu/SH}$$

Heat out, in bottoms:

$$q_{HAc} = (1782)(0.557)(245 - 183) = \frac{61{,}600 \text{ Btu}}{\text{SH}}$$

Heat out, in distillate = 0.

Heat out, in condenser water:

The reflux ratio is 15.59; therefore latent heat must be removed from 16.59 times the amount of distillate.

$$(16.59)(175 \text{ lb})\left(\frac{150 \text{ Btu}}{\text{lb}}\right) = \frac{436{,}000 \text{ Btu}}{\text{SH}}$$

$$436{,}000 + 61{,}600 - 50{,}600 = \frac{447{,}000 \text{ Btu must be added in the reboiler}}{\text{SH}}$$

PROBLEMS

6-1. A coal analysis shows 78%w C, 8% H, 5% 0, 3% N, 2% S, and 4% ash. A proximate analysis of the same coal (on the same basis) indicates 65% FC and 4.5% moisture. What is the ultimate (elemental) analysis of the VCM?

6-2. The partial ultimate analysis of a coal is as follows:

C	78%w
H	
O	
N	2%
S	2%
Ash	4%

Theoretically, 14,690 ft³ of dry air at 70°F and 740 mm Hg is required for complete combustion of 100 lb of this coal (neglecting nitrogen and sulfur). Complete the ultimate analysis.

6-3. An equimolar mixture of methane and ethane is burned with dry air. Because of a faulty jet, only 50% of the carbon is burned to CO_2, the rest going to CO. One hundred per cent excess air is supplied.

a. How many moles of air are supplied per mole of gas mixture?

b. Assuming reactants and products at "room temperature" and all water formed

condensed (conditions for a calorimeter used to determine heating values of gases), calculate the ratio of heat given off to that which would have been given off had the combustion been complete.

6-4 A fuel gas containing 30%v CH_4, 30% H_2, 10% CO, and 30% N_2 is burned with 20% excess air. The partial pressure of water vapor in the fuel gas is 13 mm Hg, and in the air it is 20 mm Hg. The total pressure of both the air and fuel gas is 760 mm Hg.

a. What is the analysis of the dry flue gas if 10% of the carbon in the flue gas is in CO?

b. What is the partial pressure of water vapor in the flue gas if the gas temperature is 600°F and the gas pressure is measured as a draft of 6 in. of water with the barometer at 760 mm Hg?

c. How many Btu's are released per 100 lbmole of dry inlet fuel gas, if it is assumed that all reactants enter at 70°F? (Note that water leaving is all in the vapor state.)

6-5. In an experiment, pure carbon is burned with an enriched air consisting of 50%m O_2 and 50%m N_2. Because of faulty combustion, not all the carbon burns. Of that which does burn, three times as much goes to form CO as that which goes to CO_2. The theoretical excess of oxygen is 10%. It is known that 51.3 liters of combustion gases, measured at 27°C and 1 atm, are formed for 10 g of carbon supplied (not all burned). What percentage of the carbon is unburned?

6-6. Pure methane, CH_4, is burned with dry air. The flue-gas analysis shows 7.49% CO_2, 1.89% CO, 4.80% O_2, and 85.82% N_2. The flue gases leave at 275°F and are 5% saturated with water vapor. The vapor pressure of water at 275°F is 2310 mm Hg. Calculate the cubic feet of wet flue gas leaving the furnace per mole of methane fired. (All the methane is burned.)

6-7. A furnace is fired with a coal containing negligible nitrogen and sulfur, whose proximate analysis indicates 4.7% moisture, 24.3% VCM, and 61.4% FC. The heating value of the coal is 14,800 Btu/lb as fired. The proximate analysis of the refuse indicates that it contains negligible moisture, 28% FC, and 65% ash. Pure carbon has a heating value of 14,550 Btu/lb. What percentage of the heating value of the fuel fired is lost in the refuse?

6-8. A coal with a heating value of 14,000 Btu/lb is burned in a furnace. The proximate analyses of the coal and refuse are as follows:

	Coal	Refuse
FC	60	36
VCM	25	7.5
Moisture	5	20.5
Ash	10	36

What percentage of the heating value of the coal fired is lost in the refuse?

6-9. Hydrogen-free coke is burned with dry air. A technician reports the flue-gas analysis as 15% CO_2, 18% CO, 7% O_2, and 60% N_2. Prove by means of appropriate calculations that the analysis is impossible.

6-10. A coke containing 96% C and 4% ash is completely burned with dry air at 70°F. The flue gases contain, on a dry basis, 1.6% CO, 11.2% CO_2, 8.8% O_2, and 78.4% N_2. These gases leave at 700°F. The average C_p of the gas is 7.3 Btu/(lbmole)(F°), and the heat of combustion of CO is 68,000 Chu/lbmole. Calculate the heat lost up the stack per pound of coke by

a. Sensible heat in the flue gas

b. Unburned CO

6-11. A fuel gas consisting entirely of methane, CH_4, and ethane, C_2H_6, is burned with air to yield a flue gas whose Orsat analysis is 10.57% CO_2, 3.79% O_2, and 85.64% N_2.

a. Calculate the analysis of the fuel in mole per cent.

b. Calculate the per cent excess air.

6-12. A coal containing 80% C is completely burned in a furnace. The flue-gas analysis shows 14.5% CO_2, 3.76% O_2, and no CO. What is the percentage of net hydrogen in the coal?

6-13. A flue-gas analysis shows 12.4% CO_2, 3.1% CO, 5.4% O_2, and 79.1% N_2. All the hydrogen but only 85% of the carbon in the fuel appear in the flue gas. Calculate the per cent excess air.

6-14. A coke containing 84% C, 4% moisture, and 12% ash is burned with dry air. On a dry basis, 33,400 ft^3 of flue gas, measured at 640°F and 730 mm Hg, is produced per 100 lb of coke. The Orsat analysis of the dry flue gas is 14.3% CO_2, 2.1% CO, 5.25% O_2, and 78.35% N_2. Some carbon is lost in the refuse. Calculate the following:

a. The refuse analysis

b. The volume of wet flue gas on the basis of 100 lb of coke

c. The net heating value of 100 lb of coke, based on evaporation of all moisture present, and assuming the heating value of coke equivalent to the heat of combustion of the carbon that it contains

d. The percentage heat loss due to unburned combustible material in the refuse

e. The percentage heat loss due to CO

f. The percentage heat loss due to sensible heat in the outlet gases, assuming an inlet temperature of 60°F

6-15. In order to increase the heating value per unit volume in a gas-fired furnace, a mixture of natural gas and producer gas is burned. The following analyses were obtained on the gases entering and leaving the furnace:

Component	Natural gas	Producer gas	Flue gas
CO_2	....	7.5	10.05
O_2	....	0.5	2.18
CO	....	20.4	2.54
H_2	....	12.4	
CH_4	85.0	3.4	
C_2H_6	10.0		
N_2	5.0	55.8	85.23

Calculate the following:

a. The pounds of producer gas supplied per pound of natural gas

b. The per cent excess air

c. The dew point of the flue gas

6-16. A coal consisting of 72% C, 10% ash, negligible nitrogen and sulfur, and the remainder net hydrogen and water (combined and moisture) is burned completely with dry air. The Orsat analysis of the flue gases is 8.50% CO_2, 4.25% CO, 7.45% O_2, and 79.8% N_2. The flue gases leave at 750 mm Hg. Calculate the following:

a. The net hydrogen and water in the coal

b. The partial pressure of water in the flue gases

c. The per cent excess air

6-17. A stoker-fired furnace is burning dry coke. One hundred and thirty-nine pounds of refuse, containing 54.5% C and 45.5% ash, is discharged per hour. The Orsat analysis of the flue gas is 10.5% CO_2, 2.1% CO, 6.7% O_2, and 80.7% N_2. The flue gas is cooled to 100°F, dried completely, and metered at 1 atm pressure, and 122,200 ft^3 of the cool, dry flue gases are formed per hour. Calculate the analysis of the dry coke (carbon, hydrogen, and ash).

6-18. Dry coke containing 4% ash, 90% C, and 6% H is burned with dry air. The flue-gas analysis is 9.6% CO_2, 1.6% CO, 8.8% O_2, and 80.0% N_2. The refuse contains 60% C and 40% ash. Calculate the following:

a. The per cent excess air

b. The volume of wet flue gas at 400°F and 730 mm Hg produced per 100 lb of coke

c. The partial pressure of water vapor in the wet flue gas

6-19. A boiler furnace is fired with a dry natural gas containing only carbon and hydrogen. The flue-gas analysis is 10.5% CO_2, 0.8% CO, 3.0% O_2, and 85.7% N_2. The air enters at 80°F, 740 mm Hg, with a relative humidity of 55%. Flue gas leaves at 700°F and 740 mm Hg. The vapor pressure of water at 80°F is 26.3 mm Hg. Calculate the following:

a. The weight analysis of the fuel

b. The per cent excess air

c. The cubic feet of air (including water) per pound of fuel

d. The cubic feet of flue gas (including water) per pound of fuel

e. The analysis of the fuel, assuming it to consist entirely of methane and ethane

f. The gross heating value of the fuel, based on a gas-industry standard cubic foot, evaluated at 60°F, 30 in. Hg, and saturated with water vapor

6-20. A furnace burns a petroleum coke containing 90% C, 2% H, 3% ash, and 5% moisture. Excess air for combustion is maintained at 20%, and 5% of the carbon and hydrogen in the fuel is lost unburned in the refuse. Eight per cent of the carbon in the flue gas is present as carbon monoxide. The air used for combustion contains water vapor at a pressure of 10 mm Hg, and the barometric pressure is 740 mm Hg. Calculate the following:

a. The analysis of the dry flue gas

b. The mole of wet flue gas per pound of coke fired

6-21. A furnace is fired with coal of the following analysis: 60% C, 14% H, 16% O, 10% ash, and negligible nitrogen and sulfur. The proximate analysis is 40% FC, 41% VCM, 9% moisture, and 10% ash. The refuse has the following analysis: 40% FC, 60% ash. It is dry. Eighteen thousand and two hundred cubic feet of wet air at a total pressure of 750 mm Hg and a temperature of 70°F, with a partial pressure of water of 10 mm Hg, is supplied per 100 lb of coal fired. The total pressure of the hot wet flue gas is 750 mm Hg. The ratio mole CO_2/mole CO is 4:1. Calculate the following:

a. The per cent excess air

b. Orsat analysis of the flue gas

c. The partial pressure of water vapor in the hot wet flue gas

6-22. A coal containing 78.76% C, 0.78% S, 1.30% N, and 6.18% ash as fired is burned at a rate of 1200 lb/hr. The proximate analysis of the coal as fired is 1.44% moisture, 34.61% VCM, 57.77% FC, and 6.18% ash. The refuse contains 21% FC, 4% VCM, and 75% ash. Air at 70°F and 29.7 in. Hg is supplied to the blower of the furnace at a rate of 4680 ft^3/min. The partial pressure of water vapor in it is 0.542 in. Hg. The flue gases contain 10.8% CO_2 and 0.2% CO on a dry basis. They leave

the furnace at 1000°F and 29.74 in. Hg. The partial pressure of water vapor in them is 1.57 in. Hg. Neglect the nitrogen and sulfur in the coal, and calculate the following:

a. Pounds of carbon lost per 100 lb of coal fired

b. Cubic feet of flue gas per minute

c. The Orsat analysis of the flue gas

6-23. A steam boiler is fired with a coal having a gross heating value of 12,470 Btu/lb. It contains 3.89%w moisture, 4.41% H, 5.47% O, 0.98% N, 0.78% S, 70.04% C, and 14.43% ash. The refuse contains no combustible matter. The wet air supplied enters the furnace at a temperature of 90°F and an absolute pressure of 760 mm Hg. Four hundred and eighty-five cubic feet of wet flue gas at a temperature of 800°F and a pressure equivalent to 3 in. H_2O draft leaves the furnace per pound of coal fired. The Orsat analysis of the flue gas is 10% CO_2, 2.4% CO, 8.0% O_2, and 79.6% N_2. The partial pressure of water vapor in the hot flue gas is 60.5 mm Hg. Barometric pressure is 760 mm Hg. Neglecting nitrogen and sulfur in the coal, calculate the following:

a. The percentage of net hydrogen in the coal

b. The moles of dry flue gas per pound of coal fired

c. The cubic feet of wet air supplied per pound of coal fired

d. A complete material balance on the furnace

e. A complete heat balance on the furnace

6-24. A pyrites burner produces gas whose analysis indicates 9.32% SO_2, 6.93% O_2, and 83.75% N_2. What percentage of the sulfur burned is converted to SO_3?

6-25. Pyrites fines, containing 88.6% FeS_2 and 11.4% gangue, are charged to a burner. An analysis of the cinder shows 81.71% Fe_2O_3, 2.19% FeS_2, and 16.1% gangue. Twenty per cent excess air is supplied based on conversion to SO_3. The burner gas is passed directly to a converter. Ninety-six per cent of the sulfur burned is converted to SO_3 in the burner and converter. What is the converter-gas analysis?

6-26. A cinder containing 84.7% Fe_2O_3 and 15.3% gangue results from the combustion of pyrites containing 89.2% FeS_2 and 10.8% gangue. Sixteen poundmole of air is supplied to the burner per 100 lb of pyrites. The burner gases pass through a converter, the effluent gas from which shows 92.6% N_2 by an Orsat analysis. Calculate the percentage of the sulfur charged that is converted to SO_3.

6-27. Dry pyrites fines containing 47% S are burned in a Herreschoff burner. The cinder produced contains 3%w SO_3. If the pyrites consist of FeS_2 and gangue, how many pounds of SO_3 are in the cinder per 100 lb of pyrites fired?

6-28. Pure sulfur is burned with 20% excess air based on conversion to SO_3. Thirty per cent of the sulfur forms SO_3; the remainder forms SO_2.

a. What is the analysis of the burner gas?

b. The burner gas is passed through a converter. If the gases leaving the converter have a mole fraction of oxygen of 0.043, what is the ratio of mole SO_3 to mole SO_2 in them?

6-29. A burner-converter chain burning pure sulfur produces a converter gas which shows 90% N_2 on analysis. Ninety per cent of the sulfur burned is converted to SO_3. Calculate the per cent excess air, based on conversion to SO_3.

6-30. Sulfur of 98% purity is burned to produce a burner gas with the following analysis: 16% SO_2, 5% O_2, and 79% N_2. The burner gas is passed to a converter where secondary air at 745 mm Hg pressure and 400°F is added to aid in conversion to SO_3. The converter gas contains 7.25% SO_3, 3.90% SO_2, 6.97% O_2, and 81.88% N_2. Calculate the volume of secondary air supplied per 100 lb of charge.

6-31. The analysis of gases from the first converter of a contact sulfuric acid plant is 4% SO_2, 13% O_2, and 83% N_2. The analysis of gases from a second converter in

series with the first is 0.45% SO_2, 11.85% O_2, and 87.7% N_2. What percentage of the SO_2 entering the second converter is converted to SO_3?

6-32. One hundred mole per hour of an SO_3-free burner gas enters a converter. The analysis of the entering gas shows 10% SO_2 and 5% O_2. If the exit gas contains 1% SO_2 (on an SO_3-free basis), what is its composition, expressed as mole per cent of SO_3, SO_2, O_2, and N_2?

6-33. One hundred pounds per hour of pyrites containing 90% FeS_2 and 10% gangue are burned with 20% excess air based on conversion to SO_3. The cinder discharged from the burner contains no sulfur. No conversion to SO_3 occurs in the burner. The burner gas is passed through a converter which effects a 98% conversion of SO_2 to SO_3. The converter gas is passed to an absorber where all the SO_3 is absorbed by 80%w sulfuric acid, which becomes 100%w sulfuric acid in the process. Calculate the following:

a. The burner-gas analysis

b. The converter-gas analysis

c. The absorber-gas analysis (gas leaving absorber)

d. The pounds of 100%w H_2SO_4 produced per 24-hr day

6-34. Dry pyrites containing 48% S is burned in a sulfuric acid manufacturing plant. The cinder contains 2% S. All this sulfur is present in SO_3 adsorbed on the cinder. The analysis of the gas leaving the sulfur burner is as follows: 8.25% SO_2, 7.85% O_2, and 83.90% N_2. After the burner gas is passed through a converter, the SO_3 is absorbed in an absorber which uses 76.1%w H_2SO_4 and produces 100%w H_2SO_4. The exit gas contains no SO_3 and has the following analysis: 0.93% SO_2, 4.68% O_2, and 94.39% N_2. Assuming that there is no conversion of SO_2 to SO_3 in the absorber, calculate the following, on the basis of 100 lb of pyrites fired:

a. Mole SO_3 in the burner gas

b. Analysis of the converter gas on an SO_3-free basis

c. Pounds of 100%w H_2SO_4 leaving the absorber

d. The heat released in the absorber at standard conditions

6-35. A chamber-process sulfuric acid plant produces SO_2 by burning pyrites that contains 46.5% sulfur. The cinders are analyzed and found to contain 2.03% S as SO_3. The burner-gas analysis averages 9.58% SO_2 and 7.51% O_2. The gas issuing from the first chamber has an average analysis of 4.87% SO_2, 5.37% O_2, and 89.76% N_2. Calculate the following:

a. The percentage of the sulfur fired that leaves the burner as SO_3 in the burner gas

b. The percentage of the sulfur fired that is converted from SO_2 into H_2SO_4 in the first chamber, assuming that the exit gas from this chamber contains no SO_3

c. The total pounds of H_2SO_4 (60% by weight) that would be produced per 24-hr day from the SO_3 in the burner gas and the SO_2 oxidized in the first chamber, if the firing rate is 600 lb of pyrites per hour

6-36. A mixture of pure sulfur and of pyrites analyzing 85% FeS_2 and 15% gangue is burned in a standard pyrites burner. The burner gas contains 10% SO_2, 7% O_2, and 83% N_2 on an SO_3-free basis and contains 1 mole SO_3/100 mole SO_3-free burner gas. The cinder contains 2% S as SO_3. Calculate the percentage of FeS_2 in the charge.

6-37. The feed to a burner is a mixture of pyrites and pure sulfur. The pyrites used is 90% FeS_2. Six per cent of the total sulfur is supplied by the pure sulfur. The cinder contains 6% S. Forty per cent of the sulfur in the cinder is in SO_3; the remainder is in unoxidized FeS_2. The burner-gas analysis is 4.25% SO_2, 8.95% O_2, and 86.80% N_2. Calculate the following:

a. The pounds of cinder formed per 100 lb of mixed charge

b. The percentage of the total sulfur charged that leaves as SO_3 in the burner gas

POSTSCRIPT

One distinguishing characteristic of an individual who has achieved a high degree of proficiency in a particular subject is the sense of integration which he displays. He recognizes the connective principles that join the parts into a whole, he recognizes the boundaries and limits of the whole, and he appreciates the relationships of the whole subject to other subjects. If a subject is very limited in scope, an individual may be unable to attain any significant proficiency in the absence of a sense of integration. But if the subject is very broad in scope, incorporating many different disciplines, he may become moderately proficient and still lack this sense. The attainment of it is a sign of maturity in understanding the subject. The basic purpose of this text is to help you mature with respect to its subject, stoichiometry. It attempts, first of all, to review significant phases of the primary disciplines involved, to integrate these disciplines into what are commonly called "stoichiometric calculations," and finally to relate these calculations to the broader subjects of industrial chemistry and chemical engineering. A secondary purpose of this text is to start you on the road to attainment of a sense of integration about chemical engineering. Therefore a brief discussion of this subject is included, and in addition to indicating the role of stoichiometry in this field, we have mentioned, whenever feasible, the other disciplines essential to chemical-engineering calculations.

The highly proficient individual displays his sense of integration with respect to the solution of a complicated problem by his ability to present a verbal description of the solution process.

A purely mathematical expression of the solution has a significant weakness. This weakness is that every step in the solution seems equally important when expressed mathematically. The verbal approach emphasizes the most important connective steps, thereby complementing the mathematical approach.

We have therefore presented numerous verbal descriptions of solution processes. You should attempt to outline your own solutions in an analogous manner before beginning the calculations.

In addition to all the other good habits that we have urged you to form, permit us to add this most mature one—the habit of conscious search for integrating factors.

Appendix A

CONVERSION FACTORS

MASS

English (all avoirdupois)

1 oz	16 drams
1 lb	16 oz
1 lb	7000 grains
1 short ton	2000 lb
1 long ton	2240 lb

Metric

1 microgram (μg)	10^{-6} g
1 milligram (mg)	10^{-3} g
1 centigram (cg)	0.01 g
1 decigram (dg)	0.1 g
1 kilogram (kg)	1000 g
1 metric ton	10^{6} g 10^{3} kg

Mixed

1 lb	453.59 g
1 metric ton	2205 lb
1 kg	2.205 lb

LENGTH

English

1 ft	12 in.
1 yd	3 ft
1 mile	5280 ft

Metric

1 centimeter (cm)	10 mm
1 decimeter (dm)	10 cm
1 meter (m)	10 dm
1 kilometer (km)	1000 m

Mixed

1 in	2.540 cm
1 m	39.37 in.

AREA

English

1 ft^2	144 in.^{2}
1 acre	43,560 ft^2
1 square mile	640 acres

APPENDIX A (*Continued*)

Metric

1 mm^2	0.01 cm^2
1 cm^2	0.01 dm^2
1 dm^2	0.01 m^2

Mixed

1 m^2	10.76 ft^2
1 m^2	1550 $in.^2$
1 $in.^2$	6.452 cm^2
1 ft^2	929 cm^2

VOLUME

English

1 ft^3	1728 $in.^3$
1 gal	4 qt
1 ft^3	7.481 gal
1 gal	231 $in.^3$
1 drum	55 gal
1 oil bbl	42 gal
1 U.S. bbl	31.5 gal

Metric

1 mm^3	10^{-6} liter 10^{-3} cm^3
1 cm^3	10^{-3} liter 10^{-3} dm^3
1 dm^3	0.1 liter 10^{-3} m^3
1 milliliter (ml)	10^{-3} liter
1 centiliter (cl)	10^{-2} liter
1 deciliter (dl)	0.1 liter

Mixed

1 ft^3	28.32 liters
1 liter	61.02 $in.^3$

TIME

English and metric

1 min	60 sec
1 hr	60 min

PRESSURE

Values equivalent to 1 atm

14.70 lb/$in.^2$
2117 lb/ft^2
10,333 kg/m^2
760 mm Hg (0°C)
33.93 ft H_2O (15°C)

HEAT, ENERGY, AND WORK

1 joule	10^7 ergs
1 (ft)(lb)	1.356 joules
1 kw-hr	2.655×10^6 (ft)(lb)
1 kw-hr	1.341 (hp)(hr)
1 Btu	252 g-cal
1 Btu	778.16 (ft)(lb)

APPENDIX A (*Continued*)

POWER

1 hp.....550 (ft)(lb)/sec
1 kw.....737.56 (ft)(lb)/sec

STANDARD GRAVITATION CONSTANT

32.1740 ft/sec^2
980.665 cm/sec^2

PERFECT-GAS-LAW CONSTANT, R

0.08206	(atm)(liter)/(gmole)(°K)
82.06	(atm)(cm^3)/(gmole)(°K)
62.36	(mm Hg)(liter)/(gmole)(°K)
1.314	(atm)(ft^3)/(lbmole)(°K)
998.9	(mm Hg)(ft^3)/(lbmole)(°K)
554.9	(mm Hg)(ft^3)/(lbmole)(°R)
0.7303	(atm)(ft^3)/(lbmole)(°R)
10.73	(lb/in.^{2})(ft^3)/(lbmole)(°R)
1545	(lb/ft^2)(ft^3)/(lbmole)(°R) = 1545 (ft)(lb)/(lbmole)(°R)
1.986	Btu/(lbmole)(°R)
1.986	cal/(gmole)(°K)

Appendix B

INTERNATIONAL ATOMIC WEIGHTS, 1954

Substance	Symbol	Atomic weight	Atomic number
Actinium	Ac	227	89
Aluminum	Al	26.98	13
Americium	Am	243	95
Antimony	Sb	121.76	51
Argon	A	39.944	18
Arsenic	As	74.91	33
Astatine	At	210	85
Barium	Ba	137.36	56
Beryllium	Be	9.013	4
Bismuth	Bi	209.00	83
Boron	B	10.82	5
Bromine	Br	79.916	35
Cadmium	Cd	112.41	48
Calcium	Ca	40.08	20
Carbon	C	12.011	6
Cerium	Ce	140.13	58
Cesium	Cs	132.91	55
Chlorine	Cl	35.457	17
Chromium	Cr	52.01	24
Cobalt	Co	58.94	27
Copper	Cu	63.54	29
Curium	Cm	245	96
Dysprosium	Dy	162.46	66
Erbium	Er	167.2	68
Europium	Eu	152.0	63
Fluorine	F	19.00	9
Francium	Fr	223	87
Gadolinium	Gd	156.9	64
Gallium	Ga	69.72	31
Germanium	Ge	72.60	32
Gold	Au	197.0	79
Hafnium	Hf	178.6	72

APPENDIX B (*Continued*)

Substance	Symbol	Atomic weight	Atomic number
Helium	He	4.003	2
Holmium	Ho	164.94	67
Hydrogen	H	1.0080	1
Indium	In	114.76	49
Iodine	I	126.91	53
Iridium	Ir	192.2	77
Iron	Fe	55.85	26
Krypton	Kr	83.80	36
Lanthanum	La	138.92	57
Lead	Pb	207.21	82
Lithium	Li	6.940	3
Lutetium	Lu	174.99	71
Magnesium	Mg	24.32	12
Manganese	Mn	54.94	25
Mercury	Hg	200.61	80
Molybdenum	Mo	95.95	42
Neodymium	Nd	144.27	60
Neon	Ne	20.183	10
Neptunium	Np	237	93
Nickel	Ni	58.69	28
Niobium	Nb	92.91	41
Nitrogen	N	14.008	7
Osmium	Os	190.2	76
Oxygen	O	16.0000	8
Palladium	Pd	106.7	46
Phosphorus	P	30.975	15
Platinum	Pt	195.23	78
Plutonium	Pu	242	94
Polonium	Po	210	84
Potassium	K	39.100	19
Praseodymium	Pr	140.92	59
Promethium	Pm	145	61
Protactinium	Pa	231	91
Radium	Ra	226.05	88
Radon	Rn	222	86
Rhenium	Re	186.31	75
Rhodium	Rh	102.91	45
Rubidium	Rb	85.48	37
Ruthenium	Ru	101.1	44
Samarium	Sm	150.43	62
Scandium	Sc	44.96	21
Selenium	Se	78.96	34
Silicon	Si	28.09	14
Silver	Ag	107.880	47
Sodium	Na	22.991	11
Strontium	Sr	87.63	38

APPENDIX B (*Continued*)

Substance	Symbol	Atomic weight	Atomic number
Sulfur	S	32.066	16
Tantalum	Ta	180.95	73
Technetium	Tc	99	43
Tellurium	Te	127.61	52
Terbium	Tb	158.93	65
Thallium	Tl	204.39	81
Thorium	Th	232.05	90
Thulium	Tm	168.94	69
Tin	Sn	118.70	50
Titanium	Ti	47.90	22
Uranium	U	238.07	92
Vanadium	V	50.95	23
Wolfram	W	183.92	74
Xenon	Xe	131.3	54
Ytterbium	Yb	173.04	70
Yttrium	Y	88.92	39
Zinc	Zn	65.38	30
Zirconium	Zr	91.22	40

Appendix C

PROPERTIES OF SATURATED STEAM*

Temp, °F	Abs. pressure, lb/in.²	Volume, ft³/lb		Enthalpy, Btu/lb	
		Liquid, v_f	Vapor, v_g	Liquid, h_f	Vapor, h_g
32	0.08854	0.01602	3306.	0.00	1075.8
35	0.09995	0.01602	2947.	3.02	1077.1
40	0.12170	0.01602	2444.	8.05	1079.3
45	0.14752	0.01602	2036.4	13.06	1081.5
50	0.17811	0.01603	1703.2	18.07	1083.7
60	0.2563	0.01604	1206.7	28.06	1088.0
70	0.3631	0.01606	867.9	38.04	1092.3
80	0.5069	0.01608	633.1	48.02	1096.6
90	0.6982	0.01610	468.0	57.99	1100.9
100	0.9492	0.01613	350.4	67.97	1105.2
110	1.2748	0.01617	265.4	77.94	1109.5
120	1.6924	0.01620	203.27	87.92	1113.7
130	2.2225	0.01625	157.34	97.90	1117.9
140	2.8886	0.01629	123.01	107.89	1122.0
150	3.718	0.01634	97.07	117.89	1126.1
160	4.741	0.01639	77.29	127.89	1130.2
170	5.992	0.01645	62.06	137.90	1134.2
180	7.510	0.01651	50.23	147.92	1138.1
190	9.339	0.01657	40.96	157.95	1142.0
200	11.526	0.01663	33.64	167.99	1145.9
210	14.123	0.01670	27.82	178.05	1149.7
212	14.696	0.01672	26.80	180.07	1150.4
220	17.186	0.01677	23.15	188.13	1153.4
230	20.780	0.01684	19.382	198.23	1157.0
240	24.969	0.01692	16.323	208.34	1160.5

APPENDIX C (*Continued*)

Temp, °F	Abs. pressure, lb/in.²	Volume, ft³/lb		Enthalpy, Btu/lb	
		Liquid, v_f	Vapor, v_g	Liquid, h_f	Vapor, h_g
250	29.825	0.01700	13.821	216.48	1164.0
260	35.429	0.01709	11.763	228.64	1167.3
270	41.858	0.01717	10.061	238.84	1170.6
280	49.203	0.01726	8.645	249.06	1173.8
290	57.556	0.01735	7.461	259.31	1176.8
300	67.013	0.01745	6.466	269.59	1179.7
310	77.68	0.01755	5.626	279.92	1182.5
320	89.66	0.01765	4.914	290.28	1185.2
330	103.06	0.01776	4.307	300.68	1187.7
340	118.01	0.01787	3.788	311.13	1190.1
350	134.63	0.01799	3.342	321.63	1192.3
360	153.04	0.01811	2.957	332.18	1194.4
370	173.37	0.01823	2.625	342.79	1196.3
380	195.77	0.01836	2.335	353.45	1198.1
390	220.37	0.01850	2.0836	364.17	1199.6
400	247.31	0.01864	1.8633	374.97	1201.0
410	276.75	0.01878	1.6700	385.83	1202.1
420	308.83	0.01894	1.5000	396.77	1203.1
430	343.72	0.01910	1.3499	407.79	1203.8
440	381.59	0.01926	1.2171	418.90	1204.3
450	422.6	0.0194	1.0993	430.1	1204.6
460	466.9	0.0196	0.9944	441.4	1204.6
470	514.7	0.0198	0.9009	452.8	1204.3
480	566.1	0.0200	0.8172	464.4	1203.7
490	621.4	0.0202	0.7423	476.0	1202.8
500	680.8	0.0204	0.6749	487.8	1201.7
520	812.4	0.0209	0.5594	511.9	1198.2
540	962.5	0.0215	0.4649	536.6	1193.2
560	1133.1	0.0221	0.3868	562.2	1186.4
580	1325.8	0.0228	0.3217	588.9	1177.3
600	1542.9	0.0236	0.2668	617.0	1165.5
620	1786.6	0.0247	0.2201	646.7	1150.3
640	2059.7	0.0260	0.1798	678.6	1130.5
660	2365.4	0.0278	0.1442	714.2	1104.4
680	2708.1	0.0305	0.1115	757.3	1067.2
700	3093.7	0.0369	0.0761	823.3	995.4
705.4	3206.2	0.0503	0.0503	902.7	902.7

* Abridged from Keenan and Keyes, "Thermodynamic Properties of Steam," John Wiley & Sons, Inc., New York. Copyright, 1937, by Joseph H. Keenan and Frederick G. Keyes.

Appendix D

VAPOR PRESSURES OF PURE COMPOUNDS*

VAPOR PRESSURES OF INORGANIC COMPOUNDS ABOVE 1 ATM

Compound	Pressure, atm								
	1	2	5	10	20	30	40	50	60
	Temperature, °C								
Ammonia	−33.6	−18.7	+4.7	25.7	50.1	66.1	78.9	89.3	98.3
Carbon monoxide	−191.3	−183.5	−170.7	−161.0	−149.7	−141.9			
Carbon dioxide	−78.2	−69.1	−56.7	−39.5	−18.9	−5.3	+5.9	14.9	22.4
Carbon disulfide	46.5	69.1	104.8	136.3	175.5	201.5	222.8	240.0	256.0
Chlorine	−33.8	−16.9	+10.3	35.6	65.0	84.8	101.6	115.2	127.1
Hydrogen chloride	−84.8	−71.4	−50.5	−31.7	−8.8	+5.9	17.8	27.9	36.2
Hydrogen sulfide	−60.4	−45.9	−22.3	−0.4	+25.5	41.9	55.8	66.7	76.3
Sulfur dioxide	−10.0	+6.3	32.1	55.5	83.8	102.6	118.0	130.2	141.7
Sulfur trioxide	44.8	60.0	82.5	104.0	138.0	157.8	175.0	187.8	198.0

* Compiled from extensive tables by D. R. Stull, *Ind. Eng. Chem.*, vol. 39, p. 517, 1947, with permission of the author and publishers.

APPENDIX D (*Continued*)

VAPOR PRESSURES OF INORGANIC COMPOUNDS UP TO 1 ATM

Compound	Pressure, mm Hg									
	1	5	10	20	40	60	100	200	400	760
	Temperature, °C									
Ammonia	−109.1	−97.5	−91.9	−85.8	−79.2	−74.3	−68.4	−57.0	−45.4	−33.6
Bromine	−48.7	−32.8	−25.0	−16.8	−8.0	−0.6	+9.3	24.3	41.0	58.2
Carbon dioxide	−134.3	−124.4	−119.5	−114.4	−108.6	−104.8	−100.2	−93.0	−85.7	−78.2
Carbon disulfide	−73.8	−54.3	−44.7	−34.3	−22.5	−15.3	−5.1	+10.4	28.0	46.5
Carbon monoxide	−222.0	−217.2	−215.0	−212.8	−210.0	−208.1	−205.7	−201.3	−196.3	−191.3
Carbon tetrachloride	−50.0	−30.0	−19.6	−8.2	+4.3	12.3	23.0	38.3	57.8	76.7
Chlorine	−118.0	−106.7	−101.6	−93.3	−84.5	−79.0	−71.7	−60.2	−47.3	−33.8
Hydrogen bromide	−138.8	−127.4	−121.8	−115.4	−108.3	−103.8	−97.7	−88.1	−78.0	−66.5
Hydrogen chloride	−150.8	−140.7	−135.6	−130.0	−123.8	−119.6	−114.0	−105.2	−95.3	−84.8
Hydrogen sulfide	−134.3	−122.4	−116.3	−109.7	−102.3	−97.9	−91.6	−82.3	−71.8	−60.4
Mercury	126.2	164.8	184.0	204.6	228.8	242.0	261.7	290.7	323.0	357.0
Nitric oxide	−184.5	−180.6	−178.2	−175.3	−171.7	−168.9	−166.0	−162.3	−156.8	−151.7
Nitrogen dioxide	−55.6	−42.7	−36.7	−30.4	−23.9	−19.9	−14.7	−5.0	+8.0	21.0
Nitrogen pentoxide	−36.8	−23.0	−16.7	−10.0	−2.9	+1.8	7.4	15.6	24.4	32.4
Nitrous oxide	−143.4	−133.4	−128.7	−124.0	−118.3	−114.9	−110.3	−103.6	−96.2	−85.5
Phosphorus trichloride	−51.6	−31.5	−21.3	−10.2	+2.3	10.2	21.0	37.6	56.9	74.2
Phosphorus pentachloride	55.5	74.0	83.2	92.5	102.5	108.3	117.0	131.3	147.2	162.0
Phosphorus trioxide	.....	39.7	53.0	67.8	84.0	94.2	108.3	129.0	150.3	173.1
Phosphorus pentoxide	384	424	442	462	481	493	510	532	556	591
Sulfur	183.8	223.0	243.8	264.7	288.3	305.5	327.2	359.7	399.6	444.6
Sulfur dioxide	−95.5	−83.0	−76.8	−69.7	−60.5	−54.6	−49.6	−35.4	−23.0	−10.0
Sulfur trioxide (α)	−39.0	−23.7	−16.5	−9.1	−1.0	+4.0	10.5	20.5	32.6	44.8
Sulfur trioxide (β)	−34.0	−19.2	−12.3	−4.9	+3.2	8.0	14.3	23.7	32.6	44.8
Sulfur trioxide (γ)	−15.3	−2.0	+4.3	11.1	17.9	21.4	28.0	35.8	44.0	51.6

APPENDIX D (*Continued*)

VAPOR PRESSURES OF ORGANIC COMPOUNDS ABOVE 1 ATM

Compound	Pressure, atm								
	1	2	5	10	20	30	40	50	60
	Temperature, °C								
Methane	−161.5	−152.3	−138.3	−124.8	−108.5	−96.3	−86.3		
Ethane	−88.6	−75.0	−52.8	−32.0	−6.4	+10.0	23.6		
Propane	−42.1	−25.6	+1.4	26.9	58.1	78.7	94.8		
n-Butane	−0.5	+18.8	50.0	79.5	116.0	140.6			
Isobutane	−11.7	+7.5	39.0	66.8	99.5	120.5			
n-Pentane	36.1	58.0	92.4	124.7	164.3	191.3			
n-Hexane	68.7	93.0	131.7	166.6	209.4				
n-Heptane	98.4	124.8	165.7	202.8	247.5				
Ethylene	−103.7	−90.8	−71.1	−52.8	−29.1	−14.2	−1.5	+8.9	
Propylene	−47.7	−31.4	−4.8	+19.8	49.5	70.0	85.0		
Acetylene	−84.0	−71.6	−50.2	−32.7	−10.0	+4.8	16.8	26.8	34.8
Methylacetylene	−23.3	−7.1	+19.5	43.8	74.0	94.0	111.5	125.0	
Benzene	80.1	103.8	142.5	178.8	221.5	249.5	272.3	290.3	
Toluene	110.6	136.5	178.0	215.8	262.5	292.8	319.0		
Cyclohexane	80.7	106.0	146.4	184.0	288.4	257.5			
Methanol	64.7	84.0	112.5	138.0	167.8	186.5	203.5	214.0	224.0
Ethanol	78.4	97.5	126.0	151.8	183.0	203.0	218.0	230.0	242.0
n-Propanol	97.8	117.0	149.0	177.0	210.8	232.3	250.0		
Isopropanol	82.5	101.3	130.2	155.7	186.0	205.0	220.2	232.0	
n-Butanol	117.5	139.8	172.5	203.0	237.0	259.0	277.0		
Isobutanol	108.0	127.3	156.2	182.0	212.5	232.0	251.0		
Phenol	181.9	208.0	248.2	283.8	328.7	358.0	382.1	400.0	418.7
Dimethyl ether	−23.7	−6.4	+20.8	45.5	75.7	96.0	112.1	125.2	
Diethyl ether	34.6	56.0	90.0	122.0	159.0	183.3			
Acetone	56.5	78.6	113.0	144.5	181.0	205.0	214.5		
Acetic acid	118.1	143.5	180.3	214.0	252.0	276.5	297.0	312.5	
Propionic acid	141.1	160.0	186.0	203.5	220.0	228.0	233.0	238.0	

APPENDIX D (*Continued*)

VAPOR PRESSURES OF ORGANIC COMPOUNDS UP TO 1 ATM

Compound	Pressure, mm Hg									
	1	5	10	20	40	60	100	200	400	760
	Temperature, °C									
Methane	−205.9	−199.0	−195.5	−191.8	−187.7	−185.1	−181.4	−175.5	−168.8	−161.5
Ethane	−159.5	−148.5	−142.9	−136.7	−129.8	−125.4	−119.3	−110.2	−99.7	−88.6
Propane	−128.9	−115.4	−108.5	−100.9	−92.4	−87.0	−79.6	−68.4	−55.6	−42.1
n-Butane	−101.5	−85.7	−77.8	−68.9	−59.1	−52.8	−44.2	−31.2	−16.3	−0.5
Isobutane	−109.2	−94.1	−86.4	−77.9	−68.4	−62.4	−54.1	−41.5	−27.1	−11.7
n-Pentane	−76.6	−62.5	−50.1	−40.2	−29.2	−22.2	−12.6	+1.9	18.5	36.1
n-Hexane	−53.9	−34.5	−25.0	−14.1	−2.3	+5.4	15.8	31.6	49.6	68.7
n-Heptane	−34.0	−12.7	−2.1	+9.5	22.3	30.6	41.8	58.7	78.0	98.4
Ethylene	−168.3	−158.3	−153.2	−147.6	−141.3	−137.3	−131.8	−123.4	−113.9	−103.7
Propylene	−131.9	−120.7	−112.1	−104.7	−96.5	−91.3	−84.1	−73.3	−60.9	−47.7
Butene-1	−104.8	−89.4	−81.6	−73.0	−63.4	−57.2	−48.9	−36.2	−21.7	−6.3
Pentene-1	−80.4	−63.3	−54.5	−46.0	−34.1	−27.1	−17.7	−3.4	+12.8	30.1
Acetylene	−142.9	−133.0	−128.2	−122.8	−116.7	−112.8	−107.9	−100.3	−92.0	−84.0
Methylacetylene	−111.0	−97.5	−90.5	−82.9	−74.3	−68.8	−61.3	−49.8	−37.2	−23.3
1-Butyne	−92.5	−76.7	−68.7	−59.9	−50.0	−43.4	−34.9	−21.6	−6.9	+8.7
Benzene	−36.7	−19.6	−11.5	−2.6	+7.6	15.4	26.1	42.2	60.6	80.1
Toluene	−26.7	−4.4	+6.4	18.4	31.8	40.3	51.9	69.5	89.5	110.6
o-Xylene	−3.8	+20.2	32.1	45.1	59.5	68.8	81.3	100.2	121.7	144.4
m-Xylene	−6.9	+16.8	28.3	41.1	55.3	64.4	76.8	95.5	116.7	139.1
p-Xylene	−8.1	+15.5	27.3	40.1	54.4	63.5	75.9	94.6	115.9	138.3
Cyclohexane	−45.3	−25.4	−15.9	−5.0	+6.7	14.7	25.5	42.0	60.8	80.7
Methylcyclohexane	−35.9	−14.0	−3.2	+8.7	22.0	30.5	42.1	59.6	79.6	100.9
Methanol	−44.0	−25.3	−16.2	−6.0	+5.0	12.1	21.2	34.8	49.9	64.7
Ethanol	−31.3	−12.0	−2.3	+8.0	19.0	26.0	34.9	48.4	63.5	78.4
n-Propanol	−15.0	+5.0	14.7	25.3	36.4	43.5	52.8	66.8	82.0	97.8
Isopropanol	−26.1	−7.0	+2.4	12.7	23.8	30.5	39.5	53.0	67.8	82.5
n-Butanol	−1.2	+20.0	30.2	41.5	53.4	60.3	70.1	84.3	100.8	117.5
Isobutanol	−9.0	+11.6	21.7	32.4	44.1	51.7	61.5	75.9	91.4	108.0
Ethylene glycol	53.0	79.7	92.1	105.8	120.0	129.5	141.8	158.5	178.5	197.3
Glycerol	125.5	153.8	167.2	182.2	198.0	208.0	220.1	240.0	263.0	290.0
Phenol	40.1	62.5	73.8	86.0	100.1	108.4	121.4	139.0	160.0	181.9
Ethylene oxide	−89.7	−73.8	−65.7	−56.6	−46.9	−40.7	−32.1	−19.5	−4.9	+10.7
Dimethyl ether	−115.7	−101.1	−93.3	−85.2	−76.2	−70.4	−62.7	−50.9	−37.8	−23.7
Diethyl ether	−74.3	−56.9	−48.1	−38.5	−27.7	−21.8	−11.5	+2.2	17.9	34.6
Formaldehyde	.....	.....	−88.0	−79.6	−70.6	−65.0	−57.3	−46.0	−33.0	−19.5
Acetaldehyde	−81.5	−65.1	−56.8	−47.8	−37.8	−31.4	−22.6	−10.0	+4.9	20.2
Acetone	−59.4	−40.5	−31.1	−20.8	−9.4	−2.0	+7.7	22.7	39.5	56.5
Formic acid	−20.0	−5.0	+2.1	10.3	24.0	32.4	43.8	61.4	80.3	100.6
Acetic acid	−17.2	+6.3	17.5	29.9	43.0	51.7	63.0	80.0	99.0	118.1
Propionic acid	4.6	28.0	39.7	52.0	65.8	74.1	85.8	102.5	122.0	141.1

Appendix E

PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS*

Name	State	Formula	Formula weight	Normal melting point, °C	Normal boiling point, °C
Methane	*g*	CH_4	16.04	−182.48	−161.4
Ethane	*g*	C_2H_6	30.07	−183.23	− 88.6
Propane	*g*	C_3H_8	44.09	−187.65	− 42.2
n-Butane	*g*	C_4H_{10}	58.12	−138.33	− 0.6
Isobutane	*g*	C_4H_{10}	58.12	−159.6	− 10.0
n-Pentane	*l*	C_5H_{12}	72.15	−129.72	36.3
n-Hexane	*l*	C_6H_{14}	86.17	− 95.32	69.0
n-Heptane	*l*	C_7H_{16}	100.20	− 90.6	98.4
Ethylene	*g*	C_2H_4	28.05	−169.15	−103.9
Propylene	*g*	C_3H_6	42.08	−185.25	− 48
Butene-1	*g*	C_4H_8	56.1	−185.35	− 5
Pentene-1	*g*	C_5H_{10}	70.13	−165.27	− 30.5
Acetylene	*g*	C_2H_2	26.04	.....	− 84
Methylacetylene	*g*	C_3H_4	40.06		
1-Butyne	*g*	C_4H_6	54.09		
Benzene	*l*	C_6H_6	78.11	5.53	80.1
Toluene	*l*	C_7H_8	92.13	− 95	110.8
o-Xylene	*l*	C_8H_{10}	106.16	− 25.19	144
m-Xylene	*l*	C_8H_{10}	106.16	− 47.87	139.3
p-Xylene	*l*	C_8H_{10}	106.16	13.26	138.5
Cyclohexane	*l*	C_6H_{12}	84.16	6.67	80.74
Methylcyclohexane	*l*	C_7H_{14}	98.18	−126.6	101
Methanol	*l*	CH_4O	32.04	− 97.8	64.7
Ethanol	*l*	C_2H_6O	46.07	−114.4	78.4
n-Propanol	*l*	C_3H_8O	60.09	−127	97.8
Isopropanol	*l*	C_3H_8O	60.09	.....	82.5
n-Butanol	*l*	$C_4H_{10}O$	74.12	− 89.2	117
Isobutanol	*l*	$C_4H_{10}O$	74.12	−108	106.9

APPENDIX E (*Continued*)

Name	State	Formula	Formula weight	Normal melting point, °C	Normal boiling point, °C
Ethylene glycol	*l*	$C_2H_6O_2$	62.07	.....	197.4
Glycerol	*l*	$C_3H_8O_3$	92.09	18	290
Phenol	*c*	C_6H_6O	94.11	40.9	181.4
Ethylene oxide	*g*	C_2H_4O	44.05	−111.3	
Dimethyl ether	*g*	C_2H_6O	46.07	−138.5	− 23.7
Diethyl ether	*l*	$C_4H_{10}O$	74.12	−116.3	34.6
Formaldehyde	*g*	CH_2O	30.03	− 92	− 21
Acetaldehyde	*l*	C_2H_4O	44.05	−123.5	+ 20.2
Acetone	*l*	C_3H_6O	58.08	− 95.5	+ 56.5
Formic acid	*l*	CH_2O_2	46.03	8.4	100.8
Acetic acid	*l*	$C_2H_4O_2$	60.05	16.7	118.1
Propionic acid	*l*	$C_3H_6O_2$	74.08	− 22	141.1

* From N. A. Lange, "Handbook of Chemistry," "Handbook Publishers, Inc., Sandusky, Ohio, by permission of the publishers.

Appendix F

LATENT HEATS OF FUSION AND VAPORIZATION OF ORGANIC COMPOUNDS*

Name	ΔH of fusion,† kcal/gmole	ΔH of vaporization,‡ kcal/gmole
Methane	0.2550	1.955
Ethane	0.6838	3.514
Propane	0.842	4.487
n-Butane	1.114	5.352
Isobutane	1.085	5.089
n-Pentane	2.011	6.160
n-Hexane	3.114	6.935
n-Heptane	3.358	7.660
Ethylene	0.801	3.327
Propylene	0.718	4.402
Butene-1	0.920	5.237
Pentene-1	1.180	
Acetylene	0.600	
2-Butyne	2.207	
Benzene	2.351	7.353
Toluene	1.582	7.997
o-Xylene	3.250	8.801
m-Xylene	2.765	8.705
p-Xylene	4.090	8.620
Cyclohexane	0.637	7.204
Methylcyclohexane	1.613	7.550
Ethanol	1.187	9.410
Methanol	0.759	8.420
n-Propanol		9.876
Isopropanol	1.267	9.575
n-Butanol	2.218	10.470
Isobutanol		10.234

APPENDIX F (*Continued*)

Name	ΔH of fusion,† kcal/gmole	ΔH of vaporization,‡ kcal/gmole
Ethylene glycol	2.685	11.863
Glycerol	4.373	
Phenol	2.732	
Diethyl ether	1.745	
Formic acid	2.711	
Acetic acid	2.803	

* From John H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950.

The values for the hydrocarbons are from the tables of the American Petroleum Institute Research Project 44, National Bureau of Standards, with some from G. S. Parks and H. M. Huffman, *Ind. Eng. Chem.*, vol. 23, p. 1138, 1931.

The values for the nonhydrocarbons were recalculated from data in "International Critical Tables," vol. 5, McGraw-Hill Book Company, Inc., New York.

† Reference state is normal melting point.

‡ Reference state is normal boiling point.

Appendix G

STANDARD ENTHALPIES OF FORMATION OF ORGANIC COMPOUNDS*

Name	State	ΔH of formation at 25°C, kcal/gmole
Methane	*g*	−17.889
Ethane	*g*	−20.236
Propane	*g*	−24.820
n-Butane	*g*	−29.812
Isobutane	*g*	−31.452
n-Pentane	*g*	−35.00
n-Pentane	*l*	−41.36
n-Hexane	*g*	−39.96
n-Hexane	*l*	−47.52
n-Heptane	*g*	−44.89
n-Heptane	*l*	−53.63
Ethylene	*g*	12.496
Propylene	*g*	4.879
Butene-1	*g*	0.280
Pentene-1	*g*	−5.000
Acetylene	*g*	54.194
Methylacetylene	*g*	44.319
1-Butyne	*g*	39.70
Benzene	*g*	19.820
Benzene	*l*	11.718
Toluene	*g*	11.950
Toluene	*l*	2.867
o-Xylene	*g*	4.540
o-Xylene	*l*	−5.841
m-Xylene	*g*	4.120
m-Xylene	*l*	−6.075
p-Xylene	*g*	4.290
p-Xylene	*l*	−5.838

APPENDIX G (*Continued*)

Name	State	ΔH of formation at 25°C, kcal/gmole
Cyclohexane	*g*	−29.43
Cyclohexane	*l*	−37.34
Methylcyclohexane	*g*	−37.00
Methylcyclohexane	*l*	−45.46
Methanol	*g*	−48.08
Methanol	*l*	−57.04
Ethanol	*g*	−52.23
Ethanol	*l*	−66.35
n-Propanol	*g*	−61.17
n-Propanol	*l*	−71.87
Isopropanol	*g*	−62.41
Isopropanol	*l*	−74.32
n-Butanol	*g*	−67.81
n-Butanol	*l*	−79.61
Isobutanol	*g*	−69.05
Isobutanol	*l*	−81.06
Ethylene glycol	*g*	−92.53
Ethylene glycol	*l*	−107.91
Glycerol	*l*	−159.16
Phenol	*g*	−21.71
Phenol	*l*	−37.80
Ethylene oxide	*g*	−16.1
Dimethyl ether	*g*	−43.06
Dimethyl ether	*l*	−51.3
Diethyl ether	*l*	−65.2
Formaldehyde	*g*	−28.29
Acetaldehyde	*g*	−39.72
Acetone	*g*	−51.79
Acetone	*l*	−59.32
Formic acid	*g*	−86.67
Formic acid	*l*	−97.8
Acetic acid	*g*	−104.72
Acetic acid	*l*	−116.2
Propionic acid	*g*	−108.75
Propionic acid	*l*	−121.7

* From John H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950.

The values for nonhydrocarbons are largely from E. I. du Pont de Nemours & Company, Ammonia Department, Chemical Division Experimental Station.

The values for the hydrocarbons are from the tables of the American Petroleum Institute Research Project 44, National Bureau of Standards.

Appendix H

STANDARD ENTHALPIES OF COMBUSTION OF ORGANIC COMPOUNDS*

Name	State	Net ΔH of combustion at 25°C, kcal/gmole	Gross ΔH of combustion at 25°C, kcal/gmole
Methane	*g*	−191.759	−212.798
Ethane	*g*	−341.261	−372.820
Propane	*g*	−488.527	−530.605
n-Butane	*g*	−635.384	−687.982
Isobutane	*g*	−633.744	−686.342
n-Pentane	*g*	−782.04	−845.16
n-Pentane	*l*	−775.68	−838.80
n-Hexane	*g*	−928.93	−1002.57
n-Hexane	*l*	−921.37	−995.01
n-Heptane	*g*	−1075.85	−1160.01
n-Heptane	*l*	−1067.11	−1151.27
Ethylene	*g*	−316.195	−337.234
Propylene	*g*	−460.428	−491.987
Butene-1	*g*	−607.679	−649.757
Pentene-1	*g*	−754.25	−806.85
Acetylene	*g*	−300.096	−310.615
Methylacetylene	*g*	−442.070	−463.109
1-Butyne	*g*	−589.302	−620.86
Benzene	*g*	−757.52	−789.08
Benzene	*l*	−749.42	−780.98
Toluene	*g*	−901.50	−943.58
Toluene	*l*	−892.42	−934.50
o-Xylene	*g*	−1045.94	−1098.54
o-Xylene	*l*	−1035.56	−1088.16
m-Xylene	*g*	−1045.52	−1098.12
m-Xylene	*l*	−1035.32	−1087.92
p-Xylene	*g*	−1045.69	−1098.29
p-Xylene	*l*	−1035.56	−1088.16
Cyclohexane	*g*	−881.67	−944.79

APPENDIX H (*Continued*)

Name	State	Net ΔH of combustion at 25°C, kcal/gmole	Gross ΔH of combustion at 25°C, kcal/gmole
Cyclohexane	*l*	−873.76	−936.88
Methylcyclohexane	*g*	−1025.95	−1099.59
Methylcyclohexane	*l*	−1017.49	−1091.13

* From John H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950. Taken from the tables in Collection, Analysis, Calculation, and Compilation of Data on the Properties of Hydrocarbons, American Petroleum Institute Research Project 44, National Bureau of Standards.

Appendix I

PHYSICAL PROPERTIES OF INORGANIC COMPOUNDS*

Name	State	Formula	Formula weight	Melting point, °C	Boiling point, °C
Aluminum	*c*	Al	26.97	660	2056
Aluminum bromide	*c*	$AlBr_3$	266.72	97.5	268
Aluminum chloride	*c*	$AlCl_3$	133.34		
Aluminum hydroxide	*c*	$Al(OH)_3$	77.99		
Aluminum oxide (corundum)	*c*	Al_2O_3	101.94	2045	3000
Ammonia	*g*	NH_3	17.03	−77.1	−33.4
Ammonium bromide	*c*	NH_4Br	97.96	542 (Subl)	
Ammonium chloride	*c*	NH_4Cl	53.50	350 (Dec)	520 (Subl)
Ammonium nitrate	*c*	NH_4NO_3	80.05	169.6	210 (Dec)
Ammonium hydroxide	*aq*	NH_4OH	35.02		
Bromine	*l*	Br_2	159.83	−7.2	58.78
Calcium	*c*	Ca	40.08	851	1487
Calcium bromide	*c*	$CaBr_2$	199.91	760	810
Calcium carbonate (calcite)	*c*	$CaCO_3$	100.09	825 (Dec)	
Calcium carbonate (dolomite)	*c*	$CaCO_3 \cdot MgCO_3$	182.42	730–760 (Dec)	
Calcium hydroxide	*c*	$Ca(OH)_2$	74.10	−580 ($-H_2O$)	
Calcium sulfate	*c*	$CaSO_4$	136.14	1297	
Calcium sulfide	*c*	CaS	72.14		
Carbon (graphite)	*c*	C	12.01	3500	4200
Carbon (diamond)	*c*	C	12.01	3500	4200
Carbon monoxide	*g*	CO	28.01	−207	−192
Carbon dioxide	*g*	CO_2	44.01	−56.6 (5.2 atm)	−78.5 (Subl)
Carbon disulfide	*g*	CS_2	76.13	−112	46.3
Ferrous bromide	*c*	$FeBr_2$	375.51		
Ferric bromide	*aq*	$FeBr_3$	535.43		
Ferrous chloride	*c*	$FeCl_2$	126.76	627	1026
Ferric chloride	*c*	$FeCl_3$	162.22	282	315
Ferrous oxide	*c*	FeO	71.85	1420	
Ferric oxide	*c*	Fe_2O_3	159.7	1560 (Dec)	
Ferroso-ferric oxide	*c*	Fe_3O_4	231.55	1538 (Dec)	
Ferrous hydroxide	*c*	$Fe(OH)_2$	89.87		
Ferric hydroxide	*c*	$Fe(OH)_3$	106.87	500 ($-\frac{1}{2}H_2O$)	
Ferrous sulfide	*c*	FeS	87.91	1193	Dec

APPENDIX I (*Continued*)

Name	State	Formula	Formula weight	Melting point, °C	Boiling point, °C
Iron sulfide (pyrites)	*c*	FeS_2	119.97	1171	Dec
Ferrous sulfate	*c*	$FeSO_4$	149.91		
Ferric sulfate	*aq*, 400	$Fe_2(SO_4)_3$	399.88	480 (Dec)	
Hydrogen bromide	*g*	HBr	80.92	−86	−67
Hydrogen chloride	*g*	HCl	36.47	−111	−85
Hydrogen cyanide	*g*	HCN	27.03	−14	26
Hydrogen peroxide	*l*	H_2O_2	34.02	−0.89	151.4
Hydrogen sulfide	*g*	H_2S	34.08	−82.9	−59.6
Magnesium bromide	*c*	$MgBr_2$	343.98	711	
Magnesium carbonate	*c*	$MgCO_3$	84.43	350 (Dec)	
Magnesium chloride	*c*	$MgCl_2$	95.23	712	1412
Magnesium hydroxide (ppt)	*c*	$Mg(OH)_2$	58.34	Dec	
Magnesium nitrate	*c*	$Mg(NO_3)_2$	152.34		
Magnesium oxide	*c*	MgO	40.32	2642	3600
Magnesium sulfide	*c*	MgS	56.58		
Magnesium sulfate	*c*	$MgSO_4$	120.38		
Nitric acid	*g*	HNO_3	63.02	−42	86
Nitric oxide	*g*	NO	30.01	−161	−151
Nitrous oxide	*g*	N_2O	44.02	−90.8	−88.5
Nitrogen dioxide	*g*	NO_2	46.01	−9.3	21.3
Nitrogen tetroxide	*g*	N_2O_4	92.02	−13	30
Nitrogen pentoxide	*c*	N_2O_5	108.02	30	47
Ozone	*g*	O_3	48.00	−251	−112
Phosphorus (white)	*c*	P	30.98	44.1	280
Phosphorus (red)	*c*	P			417
Phosphorus "	*g*	P			
Phosphorus "	*l*	P			
Phosphorus tribromide	*l*	PBr_3			
Phosphorus trichloride	*g*	PCl_3	137.35	−111.8	74.2
Phosphorus pentachloride	*g*	PCl_5	208.27		160 (Subl)
Potassium	*c*	K	39.10	62.5	776
Potassium bromide	*c*	KBr	119.01	742	1383
Potassium chloride	*c*	KCl	74.56	770	1407
Potassium cyanide	*c*	KCN	65.11	623	
Potassium carbonate	*c*	K_2CO_3	138.2	897	Dec
Potassium bicarbonate	*c*	$KHCO_3$	100.11	100–200 (Dec)	
Potassium nitrate	*c*	KNO_3	101.10	129–333 (tr)	400 (Dec)
Potassium oxide	*c*	K_2O	94.19		
Potassium hydroxide	*c*	KOH	56.10	360	1327
Potassium phosphate	*aq*	K_3PO_4	212.27	1340	
Potassium sulfide	*c*	K_2S	101.3		
Potassium sulfate	*c*	K_2SO_4	174.25	1074	
Sodium bromide	*c*	NaBr	102.91	755	1390
Sodium cyanide	*c*	NaCN	49.02	563.7	1496
Sodium carbonate	*c*	Na_2CO_3	106.00	851	Dec
Sodium chloride	*c*	NaCl	58.45	800.4	
Sodium bicarbonate	*c*	$NaHCO_3$	84.01	270($-CO_2$)	
Sodium nitrate	*c*	$NaNO_3$	85.01	308	380 (Dec)
Sodium oxide	*c*	Na_2O	61.99	Subl	
Sodium peroxide	*c*	Na_2O_2	77.99	Dec	
Sodium hydroxide	*c*	NaOH	40.00	318.4	1390
Sodium phosphate	*c*	Na_3PO_4	163.97	1340	
Sodium monosulfide	*c*	Na_2S	78.05	920	
Sodium sulfite	*c*	Na_2SO_3	126.05	Dec	
Sodium sulfate	*c*	Na_2SO_4	142.05		

APPENDIX I (*Continued*)

Name	State	Formula	Formula weight	Melting point, °C	Boiling point, °C
Sulfur (rhombic)	*c*	S	32.06	112.8 (S_8)	444.6
Sulfur (monoclinic)	*c*	S	.....	119.0 (S_8)	444.6
Sulfur (λ)	*l*	S	.....	120	444.6
Sulfur	*g*	S	32.06		
Sulfur	*g*	S_2	64.12		
Sulfur tetrachloride	*l*	SCl_4	173.89	−30	−20 (Dec)
Sulfur monochloride	*l*	S_2Cl_2	135.03	−80	138
Sulfur dioxide	*g*	SO_2	64.06	−75.5	−10
Sulfur trioxide (α)	*c*	SO_3	80.06	16.83	44.6
Sulfur trioxide (β)	*c*	$(SO_3)_2$	160.12	50	
Sulfur trioxide (γ)	*c*	.....	.....	62.2	
Sulfur oxychloride	*l*	SO_2Cl_2	134.97	−54.1	69.1
Zinc bromide	*c*	$ZnBr_2$	225.21	394	650
Zinc carbonate	*c*	$ZnCO_3$	125.39	300−(CO_2)	
Zinc chloride	*c*	$ZnCl_2$	136.29	283	732
Zinc nitrate	*aq*, 400	$Zn(NO_3)_2$	189.4		
Zinc oxide	*c*, hexagonal	ZnO	81.38	1975	
Zinc hydroxide	*c*, rhombic	$Zn(OH)_2$	99.40	125 (Dec)	
Zinc sulfide	*c*, wurtzite	ZnS	97.44	1645	1185 (Subl)
Zinc sulfate	*c*	$ZnSO_4$	161.44	740 (Dec)	

* From N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, by permission of the publishers.

Appendix J

LATENT HEATS OF FUSION AND VAPORIZATION OF INORGANIC COMPOUNDS*

Name	ΔH of fusion, kcal/gmole	ΔH of vaporization, kcal/gmole
Aluminum	2.55	61.02
Aluminum bromide	2.71	5.46
Aluminum chloride	8.48	13.38
Ammonia	1.352	5.581
Ammonium nitrate	1.460	
Bromine	2.57	7.42
Calcium	2.23	36.58
Calcium bromide	4.18	
Calcium chloride	6.1	
Calcium nitrate	5.12	
Calcium oxide	12.24	
Calcium sulfate	6.7	
Calcium carbonate	12.7	
Carbon graphite	11.0	
Carbon monoxide	0.2	1.444
Carbon dioxide	1.90	6.030 (Subl)
Carbon disulfide	1.049	
Ferrous chloride	7.8	30.21
Ferric chloride	10.3	6.02
Ferrous sulfide	5.0	
Hydrogen bromide	0.575	4.21
Hydrogen chloride	0.476	3.86
Hydrogen cyanide	2.009	6.027
Hydrogen peroxide	.....	10 27
Hydrogen sulfide	0.568	4.463
Magnesium bromide	8.3	
Magnesium chloride	8.1	32.69

APPENDIX J (*Continued*)

Name	ΔH of fusion, kcal/gmole	ΔH of vaporization, kcal/gmole
Magnesium oxide	18.5	
Magnesium sulfate	3.5	
Nitric acid	0.6	
Nitrous oxide	1.563	3.950
Nitric oxide	0.550	3.307
Nitrogen tetroxide	5.54	7.04
Nitrogen pentoxide	.....	13.8 (Subl)
Ozone	.....	2.88
Phosphorus (yellow) (white)	0.615	12.52
Phosphorus (violet)	.....	25.6 (Subl)
Phosphorus (black)	.....	33.10
Phosphoric acid	2.52	
Phosphorus trichloride	.....	7.28
Potassium	0.574	18.92
Potassium bromide	5.0	37.06
Potassium chloride	6.41	38.84
Potassium carbonate	7.8	
Potassium hydroxide	2.0	30.85
Potassium phosphate	8.9	
Potassium cyanide	3.5	
Potassium nitrate	2.84	
Potassium sulfate	8.1	
Sodium bromide	6.14	37.95
Sodium cyanide	.....	37.28
Sodium carbonate	7.0	
Sodium chloride	7.22	40.81
Sodium hydroxide	2.0	
Sodium nitrate	3.76	
Sodium monosulfide	(1.20)†	
Sulfur (rhombic)	.....	20.2
Sulfur monochloride	.....	8.72
Sulfur dioxide	1.769	5.960
Sulfur trioxide (α)	2.060	10.190
Sulfur trioxide (β)	2.890	
Sulfur trioxide (γ)	6.310	
Sulfur oxychloride	.....	7.76
Water	1.436	9.729
Zinc chloride	5.50	28.71
Zinc oxide	4.47	
Zinc sulfide (wurtzite)	9.00	

* From John H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950. Most values are from the compilations by K. K. Kelley, Heats of Fusion of Inorganic Compounds, *U.S. Bur. Mines Bull.* 393, 1936, and The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances, *U.S. Bur. Mines Bull.* 383, 1935.

† ( ) signifies uncertain value.

Appendix K

STANDARD ENTHALPIES OF FORMATION OF INORGANIC COMPOUNDS*

Name	State	ΔH of formation at 25°C, kcal/gmole
Aluminum	*c*	0.00
Aluminum bromide	*c*	−123.4
Aluminum chloride	*c*	−163.8
Aluminum oxide	*c*, corundum	−399.09
Aluminum hydroxide	*c*	−304.8
Ammonia	*g*	−10.96
Ammonium bromide	*c*	−64.57
Ammonium chloride	*c*	−75.23
Ammonium nitrate	*c*	−87.40
Ammonium hydroxide	*aq*	−87.59
Bromine	*l*	0.00
Bromine	*g*	7.47
Calcium	*c*	0.00
Calcium bromide	*c*	−162.20
Calcium chloride	*c*	−190.6
Calcium carbonate	*c*, calcite	−289.5
Dolomite	*c*	−558.8
Calcium nitrate	*c*	−224.05
Calcium oxide	*c*	−151.7
Calcium hydroxide	*c*	−235.58
Calcium sulfide	*c*	−114.3
Calcium sulfate	*c*, insoluble form	−338.73
Carbon (graphite)	*c*	000.00
Carbon (diamond)	*c*	0.453
Carbon monoxide	*g*	−26.416
Carbon dioxide	*g*	−94.052
Carbon disulfide	*g*	28.11
Ferrous bromide	*c*	−57.15
Ferric bromide	*aq*	−95.5
Ferrous chloride	*c*	−81.9

APPENDIX K (*Continued*)

Name	State	ΔH of formation at 25°C, kcal/gmole
Ferric chloride	*c*	−96.4
Ferrous oxide	*c*	−64.62
Ferric oxide	*c*	−198.5
Ferroso-ferric oxide	*c*	−266.9
Ferrous hydroxide	*c*	−135.9
Ferric hydroxide	*c*	−197.3
Ferrous sulfide	*c*	−22.64
Iron sulfide	*c*, pyrites	−38.62
Ferrous sulfate	*c*	−221.3
Ferric sulfate	*aq*, 400	−653.3
Hydrogen bromide	*g*	−8.66
Hydrogen chloride	*g*	−22.063
Hydrogen cyanide	*g*	31.1
Hydrogen cyanide	*l*	25.2
Hydrogen peroxide	*l*	−45.16
Hydrogen sulfide	*g*	−4.77
Magnesium bromide	*c*	−123.9
Magnesium carbonate	*c*	−261.7
Magnesium chloride	*c*	−153.220
Magnesium nitrate	*c*	−188.770
Magnesium oxide	*c*	−143.84
Magnesium hydroxide	*c*, ppt	−221.90
Magnesium sulfide	*c*	−84.2
Magnesium sulfate	*c*	−304.94
Nitrous oxide	*g*	19.55
Nitric oxide	*g*	21.600
Nitrogen dioxide	*g*	7.96
Nitrogen tetroxide	*g*	2.23
Nitrogen pentoxide	*c*	−10.0
Nitric acid	*g*	−31.99
Nitric acid	*l*	−41.35
Ozone	*g*	33.88
Phosphorus	*c*, white	0.00
Phosphorus	*c*, red	−4.22
Phosphorus	*g*	150.35
Phosphorus tribromide	*l*	−45.
Phosphorus pentabromide	*c*	−60.6
Phosphorus trichloride	*g*	−70.0
Phosphorus trichloride	*l*	−76.8
Phosphorus pentachloride	*g*	−91.0
Phosphorus pentoxide	*c*	−360.0
Phosphoric acid	*c*	−306.2
Potassium	*c*	0.00
Potassium bromide	*c*	−94.06
Potassium chloride	*c*	−104.348
Potassium cyanide	*c*	−28.1
Potassium carbonate	*c*	−274.01
Potassium bicarbonate	*c*	−229.8
Potassium nitrate	*c*	−118.08
Potassium oxide	*c*	−86.2

APPENDIX K (*Continued*)

Name	State	ΔH of formation at 25°C, kcal/gmole
Potassium hydroxide	*c*	−102.02
Potassium phosphate	*aq*	−478.7
Potassium sulfide	*c*	−121.5
Potassium sulfate	*c*	−342.65
Sodium bromide	*c*	−86.72
Sodium cyanide	*c*	−22.47
Sodium carbonate	*c*	−269.46
Sodium chloride	*c*	−98.321
Sodium bicarbonate	*c*	−226.0
Sodium nitrate	*c*	−111.71
Sodium oxide	*c*	−99.45
Sodium peroxide	*c*	−119.2
Sodium hydroxide	*c*	−101.96
Sodium phosphate	*c*	−457.
Sodium monosulfide	*c*	−89.8
Sodium sulfite	*c*	−261.2
Sodium sulfate	*c*	−330.50
Sulfur	*c*, rhombic	0.00
Sulfur	*c*, monoclinic	−0.071
Sulfur	*l*, λ	0.257
Sulfur	*g*	53.25
Sulfur tetrachloride	*l*	−13.7
Sulfur monochloride	*l*	−14.2
Sulfur dichloride	*l*	−24.1
Sulfur monoxide	*g*	19.02
Sulfur dioxide	*g*	−70.94
Sulfur trioxide	*g*	−94.39
Sulfur trioxide	*l*	−103.03
Sulfur trioxide	*c*, α	−105.09
Sulfur trioxide	*c*, β	−105.92
Sulfur trioxide	*c*, γ	−109.34
Sulfuric oxychloride	*g*	−82.04
Sulfuric oxychloride	*l*	−89.80
Sulfurous acid	*aq*, 200	−146.88
Water	*g*	−57.798
Water	*l*	−68.317
Zinc bromide	*c*	−77.0
Zinc carbonate	*c*	−192.9
Zinc chloride	*c*	−99.9
Zinc nitrate	*aq*, 400	−134.9
Zinc oxide	*c*, hexagonal	−83.36
Zinc hydroxide	*c*, rhombic	−153.66
Zinc sulfide	*c*, wurtzite	−45.3
Zinc sulfate	*c*	−233.4

* From John H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950. Values were derived from F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, 1936; W. M. Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solution," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1938; the tables of the American Petroleum Institute Research Project 44, National Bureau of Standards; and the tables of Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards.

Appendix L

STANDARD ENTHALPIES OF FORMATION OF INORGANIC COMPOUNDS IN SOLUTION IN WATER AT 25°C AND 1 ATM PRESSURE*

Compound	Mole water / mole compound	ΔH of formation at 25°C, kcal/gmole
Aluminum bromide	....	−209.5
Aluminum chloride	600	−243.9
Ammonia	200	−19.27
Ammonium bromide	....	−60.27
Ammonium chloride	400	−71.20
Ammonium nitrate	500	−80.89
Ammonium hydroxide	....	−87.59
Calcium bromide	400	−187.19
Calcium chloride	....	−209.15
Calcium nitrate	400	−228.29
Calcium hydroxide	800	−239.2
Cupric bromide	....	−42.4
Cupric chloride	400	−64.7
Cupric nitrate	200	−83.6
Cupric sulfate	800	−200.78
Ferrous bromide	540	−78.7
Ferric bromide	....	−95.5
Ferrous chloride	....	−100.0
Ferric chloride	2000	−128.5
Ferrous sulfate	400	−236.2
Ferric sulfate	400	−653.3
Hydrogen bromide	400	−28.80
Hydrogen chloride	400	−39.85
Hydrogen cyanide	100	+24.2
Hydrogen peroxide	200	−45.80
Hydrogen sulfide	2000	−9.38

APPENDIX L (*Continued*)

Compound	Mole water / mole compound	ΔH of formation at 25°C, kcal/gmole
Magnesium bromide	400	−167.33
Magnesium chloride	400	−189.76
Magnesium nitrate	400	−209.927
Magnesium sulfide	....	−108
Magnesium sulfate	400	−325.4
Mercuric bromide	....	−38.4
Mercuric chloride	....	−50.3
Mercurous nitrate	....	−56.8
Mercuric nitrate	....	−58.5
Nitric acid	400	−49.210
Phosphoric acid	400	−309.32
Potassium bromide	400	−89.19
Potassium chloride	400	−100.164
Potassium cyanide	400	−25.3
Potassium carbonate	400	−280.90
Potassium bicarbonate	2000	−224.85
Potassium nitrate	400	−109.79
Potassium hydroxide	400	−114.96
Potassium phosphate	....	−478.7
Potassium sulfide	400	−110.75
Potassium sulfate	400	−336.48
Sodium bromide	400	−86.33
Sodium cyanide	200	−22.29
Sodium carbonate	1000	−275.13
Sodium chloride	400	−97.324
Sodium bicarbonate	....	−222.1
Sodium nitrate	400	−106.880
Sodium hydroxide	400	−112.193
Sodium phosphate	400	−471.9
Sodium monosulfide	400	−105.17
Sodium sulfite	800	−264.1
Sodium sulfate	1100	−330.82
Sulfurous acid	200	−146.88
Sulfuric acid	400	−212.03
Zinc bromide	400	−93.6
Zinc chloride	400	−115.44
Zinc nitrate	400	−134.9
Zinc sulfate	400	−252.12

* From John H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950. Values were derived from F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Chemical Elements," Reinhold Publishing Corporation, New York, 1936; W. M. Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solution," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1938; the tables of the American Petroleum Institute Research Project 44, National Bureau of Standards; and the tables of Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards.

Appendix M

HEAT CAPACITIES OF ELEMENTS AND INORGANIC COMPOUNDS*

Name	State	C_p, cal/(gmole)(C°)	Temperature range, °K
Aluminum	c	$4.80 + 0.00322T$†	273–931
Aluminum	l	7.00	931–1273
Aluminum bromide	c	$18.74 + 0.01866T$	273–370
Aluminum bromide	l	29.5	
Aluminum chloride	c	$13.25 + 0.02800T$	273–465
Aluminum chloride	l	31.2	465–504
Aluminum oxide	c	$22.08 + 0.08971T - 522{,}500/T^2$	273–1973
Ammonia	g	$6.70 + 0.00630T$	300–800
Ammonium bromide	c	22.8	274–328
Ammonium chloride	c, α	$9.80 + 0.0368T$	273–457
Ammonium chloride	c, β	$5.0 + 0.0340T$	457–523
Ammonium nitrate	c	31.8	273–293
Bromine	g	9.00	300–2000
Calcium	c	$5.31 + 0.00333T$	273–673
Calcium	c	$6.29 + 0.00140T$	673–873
Calcium chloride	c	$16.9 + 0.00386T$	273–1055
Calcium carbonate	c	$19.68 + 0.001189T - 307{,}600/T^2$	273–1033
Dolomite	c	40.1	299–372
Calcium oxide	c	$10.00 + 0.00484T - 108{,}000/T^2$	273–1173
Calcium hydroxide	c	21.4	276–373
Calcium sulfate	c	$18.52 + 0.02197T - 156{,}800/T^2$	273–1373
Carbon (graphite)		$2.673 + 0.002617T - 116{,}900/T^2$	273–1373
Carbon (diamond)	c	$2.162 + 0.003059T - 130{,}300/T^2$	273–1373
Carbon monoxide	g	$6.60 + 0.00120T$	273–2500
Carbon dioxide	g	$10.34 + 0.00274T - 195{,}500/T^2$	273–1200
Carbon disulfide	l	18.4	293
Iron	c, α	$41.3 + 0.00638T$	273–1041
Iron	c, β	$6.12 + 0.00336T$	1041–1179
Iron	c, γ	8.40	1179–1674
Iron	c, δ	10.0	1674–1803
Iron	l	8.15	1803–1873
Ferrous oxide	c	$12.62 + 0.001492T - 76{,}200/T^2$	273–1173
Ferric oxide	c	$24.72 + 0.01604T - 423{,}400/T^2$	273–1097
Ferroso-ferric oxide	c	$41.17 + 0.01882T - 979{,}500/T^2$	273–1065
Ferrous sulfide	c, α	$2.03 + 0.0390T$	273–411
Ferrous sulfide	c, β	$12.05 + 0.00273T$	411–1468

APPENDIX M (*Continued*)

Name	State	C_p, cal/(gmole)(C°)	Temperature range, °K
Iron sulfide	*c*, pyrites	$10.7 + 0.01336T$	273–773
Ferrous sulfate	*c*	22	293–373
Ferric sulfate	*c*	66.2	273–373
Hydrogen	*g*	$6.62 + 0.00081T$	273–2500
Hydrogen bromide	*g*	$6.80 + 0.00084T$	273–2000
Hydrogen chloride	*g*	$6.70 + 0.00084T$	273–2000
Hydrogen sulfide	*g*	$7.20 + 0.00360T$	300–600
Magnesium	*c*	$6.20 + 0.00133T - 67{,}800/T^2$	273–923
Magnesium	*l*	7.4	923–1048
Magnesium carbonate	*c*	16.9	290
Magnesium chloride	*c*	$17.3 + 0.00377T$	273–991
Magnesium oxide	*c*	$10.86 + 0.001197T - 208{,}700/T^2$	273–2073
Magnesium hydroxide	*c*	18.2	292–323
Magnesium sulfate	*c*	26.7	296–372
Nitrogen	*g*	$6.50 + 0.00100T$	300–3000
Nitric oxide	*g*	$8.05 + 0.000233T - 156{,}300/T^2$	300–5000
Oxygen	*g*	$8.27 + 0.000258T - 187{,}700/T^2$	300–5000
Phosphorus	*c*, white	5.50	273–317
Phosphorus	*c*, red	$0.21 + 0.0180T$	273–472
Phosphorus	*l*	6.6	317–373
Phosphorus trichloride	*l*	28.7	284–371
Potassium	*c*	$5.24 + 0.00555T$	273–336
Potassium	*l*	7.7	336–373
Potassium bromide	*c*	$11.49 + 0.00360T$	273–543
Potassium chloride	*c*	$10.93 + 0.00376T$	273–1043
Potassium carbonate	*c*	29.9	296–372
Potassium nitrate	*c*	$6.42 + 0.0530T$	273–401
Potassium nitrate	*c*	28.8	401–611
Potassium nitrate	*l*	29.5	611–683
Potassium sulfate	*c*	33.1	287–371
Sodium	*c*	$5.01 + 0.00536T$	273–371
Sodium	*l*	7.50	371–451
Sodium bromide	*c*	$11.74 + 0.00233T$	273–543
Sodium carbonate	*c*	28.9	288–371
Sodium chloride	*c*	$10.79 + 0.00420T$	273–1073
Sodium chloride	*l*	15.9	1073–1205
Sodium nitrate	*c*	$4.56 + 0.0580T$	273–583
Sodium nitrate	*l*	37.2	583–703
Sodium sulfate	*c*	32.8	289–371
Sulfur	*c*, rhombic	$3.63 + 0.00640T$	273–368
Sulfur	*c*, monoclinic	$4.38 + 0.00440T$	368–392
Sulfur (S_2)	*g*	$8.58 + 0.00030T$	300–2500
Sulfur monochloride	*l*	27.5	273–332
Sulfur dioxide	*g*	$7.70 + 0.00530T - 0.00000083T^2$	300–2500
Water	*g*	$8.22 + 0.00015T + 0.00000134T^2$	300–2500
Zinc	*c*	$5.25 + 0.00270T$	273–692
Zinc	*l*	$7.59 + 0.00055T$	692–1122
Zinc chloride	*c*	$15.9 + 0.00800T$	273–638
Zinc oxide	*c*	$11.40 + 0.00145T - 182{,}400/T^2$	273–1573
Zinc sulfide	*c*	$12.81 + 0.00095T - 194{,}600/T^2$	273–1173
Zinc sulfate	*c*	28	293–373

* From John H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950. Taken from the compilation on high-temperature specific-heat equations for inorganic substances by K. K. Kelley, *U.S. Bur. Mines Bull.* 371, 1934.

† In °K.

Appendix N

HEAT CAPACITIES OF ORGANIC COMPOUNDS*

Compound	State	t, °C	C_p, cal/(g)(C°)
Methane	g	0	0.51
		100	0.58
		200	0.67
		300	0.76
Ethane	g	0	0.43
		200	0.59
		400	0.74
		600	0.93
		1000	1.05
		1400	1.23
Propane	l	0	0.576
n-Butane	l	0	0.549
Isobutane	l	0	0.549
n-Hexane	l	−80	0.47
		−40	0.495
		0–50	0.527
		20–100	0.600
n-Heptane	l	0–50	0.507
		20	0.490
		30	0.518
Ethylene	g	0	0.36
		200	0.53
		400	0.64
		600	0.77
		1000	0.87
		1400	0.99
Acetylene	g	0	0.41
		200	0.49
		400	0.57
		600	0.59
		1000	0.65
		1400	0.71

APPENDIX N (*Continued*)

Compound	State	t, °C	C_p, cal/(g)(C°)
Benzene	c	−250	0.0399
		−200	0.124
		−100	0.227
		0	0.375
Benzene	l	10	0.342
		40	0.425
		80	0.465
Toluene	l	10	0.364
		85	0.534
		12–99	0.440
o-Xylene	l	0	0.392
		30	0.411
		60	0.434
		100	0.465
m-Xylene	l	0	0.383
		30	0.401
		60	0.426
		100	0.458
p-Xylene	l	0	0.383
		30	0.397
		60	0.425
		100	0.460
Methanol	l	−40	0.536
		0	0.575
		15–20	0.601
Ethanol	c	−190	0.232
		−130	0.376
Ethanol	l	−20	0.505
		30	0.600
		50	0.672
		80	0.778
n-Propanol	c	−200	0.170
		−175	0.363
		−130	0.497
	l	−20	0.485
		0	0.530
		50	0.650
		100	0.765
Isopropanol	l	−20	0.518
		0	0.580
		20	0.641
		50	0.733
n-Butanol	l	21–115	0.687
		−76	0.443
		0	0.52
		30	0.582
		100	0.788

APPENDIX N (*Continued*)

Compound	State	t, °C	C_p, cal/(g)(C°)
Isobutanol	l	21–109	0.716
		0	0.505
		50	0.674
		100	0.832
Ethylene glycol	l	−40	0.505
		0	0.542
		70	0.634
		140	0.709
		200	0.780
Glycerol	c	−265	0.009
		−250	0.047
		−200	0.115
		−100	0.217
		0	0.330
Glycerol	l	15–50	0.576
		0	0.545
		40	0.594
Phenol	c	14–26	0.561
Diethyl ether	l	−100	0.511
		−50	0.515
		−5	0.525
		0	0.521
		30	0.545
		80	0.687
		120	0.800
		140	0.819
		180	1.037
Acetone	l	0	0.506
		20	0.525
		50	0.549
Formic acid	l	0	0.436
		15.5	0.509
		20–100	0.524
Acetic acid	c	−100	0.250
Acetic acid	l	26–95	0.522
		20	0.485
		50	0.512
		80	0.538
Propionic acid	c	−33	0.726
Propionic acid	l	0	0.444
		20–137	0.560

* From John H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950; from "International Critical Tables," vol. 5, McGraw-Hill Book Company, Inc., New York; and a few data from other sources.

Appendix O

HEAT CAPACITIES OF AQUEOUS SOLUTIONS*

HYDROCHLORIC ACID

Mole % HCl	Specific heat, cal/(g)(C°)				
	0°C	10°C	20°C	40°C	60°C
0.0	1.00				
9.09	0.72	0.72	0.74	0.75	0.78
16.7	0.61	0.605	0.631	0.645	0.67
20 0	0.58	0.575	0.591	0.615	0.638
25.9	0.55	.....	.....	.....	0.61

SULFURIC, NITRIC, AND PHOSPHORIC ACIDS

Weight % acid	H_2SO_4, cal/(g)(C°) at 20°C	HNO_3, cal/(g)(C°) at 20°C	H_3PO_4, cal/(g)(C°) at 21.3°C
0	1.000	1.000	
10	0.916	0.900	0.928
20	0.843	0.810	0.850
30	0.768	0.730	0.773
40	0.680	0.675	0.703
50	0.597	0.650	0.635
60	0.526	0.640	0.570
70	0.475	0.615	0.516
80	0.449	0.575	0.469
90	0.432	0.515	0.420
100	0.335		

* By permission from John H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950.

APPENDIX O (*Continued*)

ACETIC ACID (AT 38°C)

Mole % acetic acid	0	6.98	30.9	54.5	100
Cal/(g)(C°)	1.00	0.911	0.73	0.631	0.535

SODIUM HYDROXIDE (AT 20°C)

Mole % NaOH	0	0.5	1.0	9.09	16.7	28.6	37.5
Cal/(g)(C°)	1.0	0.985	0.97	0.835	0.80	0.784	0.782

POTASSIUM HYDROXIDE (AT 19°C)

Mole % KOH	0	0.497	1.64	4.76	9.09
Cal/(g)(C°)	1.0	0.975	0.93	0.814	0.75

AMMONIA

Mole % NH_3	Specific heat, cal/(g)(C°)			
	2.4°C	20.6°C	41°C	61°C
0	1.01	1.0	0.995	1.0
10.5	0.98	0.995	1.06	1.02
20.9	0.96	0.99	1.03	
31.2	0.956	1.0		
41.4	0.985			

SODIUM CARBONATE

% Na_2CO_3 by weight	Temperature °C			
	17.6	30.0	76.6	98.0
0.000	0.9992	0.9986	1.0098	1.0084
1.498	0.9807			
2.000	.....	0.9786		
2.901	0.9597			
4.000	.....	0.9594		
5.000	0.9428	.....	0.9761	
6.000	.....	0.9392		
8.000	0.9183			
10.000	0.9086	.....	0.9452	
13.790	0.8924			
13.840	.....	0.8881		
20.000	.....	0.8631	0.8936	
25.000	.....	.....	0.8615	0.8911

APPENDIX O (*Continued*)

SODIUM CHLORIDE

Mole % NaCl	Specific heat, cal/(g)(C°)			
	6°C	20°C	33°C	57°C
0.249	.....	0.99		
0.99	0.96	0.97	0.97	
2.44	0.91	0.915	0.915	0.923
9.09	0.805	0.81	0.81	0.82

POTASSIUM CHLORIDE

Mole % KCl	Specific heat, cal/(g)(C°)			
	6°C	20°C	33°C	40°C
0.99	0.945	0.947	0.947	0.947
3.85	0.828	0.831	0.835	0.837
5.66	0.77	0.775	0.778	0.775
7.41	.....	0.727		

METHYL ALCOHOL (METHANOL)

Mole % CH_3OH	Specific heat, cal/(g)(C°)		
	5°C	20°C	40°C
5.88	1.02	1.0	0.995
12.3	0.975	0.982	0.98
27.3	0.877	0.917	0.92
45.8	0.776	0.811	0.83
69.6	0.681	0.708	0.726
100	0.576	0.60	0.617

ETHYL ALCOHOL (ETHANOL)

Mole % C_2H_5OH	Specific heat, cal/(g)(C°)		
	3°C	23°C	41°C
4.16	1.05	1.02	1.02
11.5	1.02	1.03	1.03
37.0	0.805	0.86	0.875
61.0	0.67	0.727	0.748
100	0.54	0.577	0.621

APPENDIX O (*Continued*)

NORMAL PROPYL ALCOHOL (*n*-PROPANOL)

Mole % C_3H_7OH	Specific heat, cal/(g)(C°)		
	5°C	20°C	40°C
1.55	1.03	1.02	1.01
5.03	1.07	1.06	1.03
11.4	1.035	1.032	0.99
23.1	0.877	0.90	0.91
41.2	0.75	0.78	0.815
73.0	0.612	0.645	0.708
100	0.534	0.57	0.621

GLYCEROL

Mole % $C_3H_5(OH)_3$	Specific heat, cal/(g)(C°)	
	15°C	32°C
2.12	0.961	0.960
4.66	0.929	0.924
11.5	0.851	0.841
22.7	0.765	0.758
43.9	0.67	0.672
100	0.555	0.576

Appendix P

MOLAL HEAT CAPACITIES AND ENTHALPIES OF GASES*

T = °R C_p = Btu/(lbmole)(F°) H = Btu/lbmole (H = 0 at 0°R)

Gas	N_2		O_2		H_2O		CO_2		H_2		CO	
T	C_p	H	C_p	H	C_p	H	C_p	H	C_p	H	C_p	H
200	6.948	.....	6.954	.....	7.946	.....	6.995	.....	5.564	.....	6.948	
250	6.948	.....	6.954	.....	7.950	.....	7.133	.....	5.935	.....	6.948	
300	6.949	2,082.0	6.954	2,073.5	7.954	2,367.6	7.367	2,108.2	6.241	2,063.5	6.949	2,081.9
350	6.950	2,429.5	6.954	2,421.3	7.958	2,765.6	7.662	2,483.6	6.476	2,381.8	6.950	2,429.4
400	6.950	2,777.0	6.956	2,769.1	7.965	3,163.8	7.987	2,874.7	6.645	2,710.2	6.951	2,776.9
450	6.951	3,124.6	6.967	3,117.2	7.978	3,562.5	8.318	3,282.3	6.764	3,045.8	6.952	3,124.5
500	6.952	3,472.2	6.988	3,466.2	7.997	3,962.0	8.642	3,706.2	6.844	3,386.1	6.954	3,472.1
550	6.956	3,819.9	7.018	3,816.4	8.024	4,362.6	8.952	4,146.0	6.896	3,729.9	6.959	3,819.9
600	6.961	4,167.9	7.058	4,168.3	8.059	4,764.7	9.242	4,600.9	6.926	4,075.6	6.967	3,168.0
650	6.969	4,516.1	7.107	4,522.4	8.104	5,168.9	9.516	5,069.8	6.945	4,422.5	6.980	4,516.6

700	6.979	4,864.9	7.165	4,879.3	8.156	5,575.4	9.775	5,552.0	6.957	4,770.2	6.998	4,866.0
750	6.994	5,214.2	7.225	5,239.1	8.212	5,984.6	10.013	6,046.7	6.967	5,118.4	7.021	5,216.5
800	7.012	5,564.4	7.289	5,602.0	8.273	6,396.9	10.237	6,552.9	6.975	5,467.1	7.049	5,568.2
850	7.036	5,915.6	7.357	5,968.3	8.339	6,812.1	10.452	7,070.0	6.981	5,816.0	7.081	5.921.5
900	7.064	6,268.1	7.426	6,337.9	8.408	7,230.9	10.655	7,597.6	6.985	6,165.3	7.118	6,276.4
1000	7.132	6,977.9	7.562	7,087.5	8.554	8,078.9	11.034	8,682.1	6.994	6,864.5	7.200	6,992.2
1100	7.209	7,695.0	7.692	7,850.4	8.707	8,942.0	11.374	9,802.6	7.004	7,564.6	7.292	7,716.8
1200	7.293	8,420.0	7.813	8,625.8	8.863	9,820.4	11.679	10,955.3	7.018	8,265.8	7.388	8,450.8
1300	7.383	9,153.9	7.922	9,412.9	9.023	10,714.5	11.954	12,136.9	7.037	8,968.7	7.486	9,194.6
1400	7.475	9,896.9	8.021	10,210.4	9.186	11,624.8	12.202	13,344.7	7.061	9,673.8	7.583	9,948.1
1500	7.564	10,648.9	8.110	11,017.4	9.353	12,551.4	12.428	14,576.0	7.090	10,381.5	7.677	10,711.1
1600	7.650	11,409.7	8.192	11,832.5	9.522	13,494.9	12.633	15,829.0	7.127	11,092.5	7.767	11,483.4
1700	7.733	12,178.9	8.266	12,655.6	9.693	14,455.4	12.818	17,101.4	7.169	11,807.4	7.850	12,264.3
1800	7.813	12,956.3	8.332	13,485.8	9.865	15,433.0	12.987	18,391.5	7.215	12,526.8	7.928	13,053.2
1900	7.890	13,741.6	8.390	14,322.1	10.035	16,427.5	13.141	19,697.8	7.264	13,250.9	8.001	13,849.8
2000	7.962	14,534.4	8.443	15,164.0	10.202	17,439.0	13.280	21,018.7	7.316	13,980.1	8.069	14,653.2
2100	8.027	15,334.0	8.492	16,010.9	10.366	18,466.9	13.407	22,352.7	7.369	14,714.5	8.132	15,463.3
2200	8.086	16,139.8	8.539	16,862.6	10.526	19,510.8	13.522	23,699.0	7.424	15,454.4	8.189	16,279.4
2300	8.140	16,951.2	8.582	17,718.8	10,682	20,570.6	13.629	25,056.3	7.479	16,199.8	8.240	17,101.0
2400	8.191	17,767.9	8.622	18.579.2	10.833	21,645.7	13.728	26,424.0	7.535	16.950.6	8.289	17,927.4
2500	.....	18,589.5	.....	19,443.4	10.978	22,735.4	13.820	27,801.2	7.592	17,707.3	8.335	18,758.8
2600	8.284	19,415.8	8.695	20,311.4	11.119	23,839.5	13.904	29,187.1	7.650	18,469.7	8.376	19,594.3
2800	8.365	21,081.1	8.764	22,057.8	11.382	26,088.0	14.056	31,982.8	7.761	20,011.8	8.449	21,277.2
3000	8.436	22,761.5	8.830	23,817.7	11.621	28,386.3	14.186	34,806.6	7.879	21,576.9	8.511	22,973.4
3200	8.496	24,455.0	8.893	25,590.5	11.841	30,730.2	14.297	37,654.7	7.987	23,164.1	8.565	24,681.2

APPENDIX P (*Continued*)

Gas	N_2		O_2		H_2O		CO_2		H_2		CO	
T	C_p	H	C_p	H	C_p	H	C_p	H	C_p	H	C_p	H
3400	8.549	26,159.7	8.956	27,375.9	12.043	33,116.0	14.396	40,523.6	8.085	24,771.9	8.614	26,399.3
3600	8.596	27,874.4	9.019	29,173.9	12.227	35,540.1	14.481	43,411.0	8.176	26,398.5	8.658	28,126.6
3800	8.638	29,597.9	9.079	30,984.1	12.393	37,998.9	14.555	46,314.0	8.261	28,042.8	8.697	29,862.3
4000	8.676	31,329.4	9.138	32,806.1	12.546	40,489.1	14.624	49.231.4	8.341	29,703.5	8.731	31,605.2
4200	8.709	33,068.1	9.196	34,639.9	12.685	43,008.4	14.688	52,162.0	8.416	31,379.8	8.760	33,354.4
4400	8.739	34,813.1	9.252	36,485.0	12.813	45,553.9	14.748	55,105.1	8.487	33,070.9	8.787	35,109.2
4600	8.766	36,563.8	9.307	38,341.4	12.980	48,123.6	14.804	58,059.7	8.554	34,775.7	8.812	36,869.3
4800	8.790	38,319.5	9.361	40,208.6	13.037	50,715.5	14.855	61,024.9	8.617	36,493.4	8.834	38,633.9
5000	8.812	40,079.8	9.413	42,086.3	13.135	53,327.4	14.902	64,000.0	8.677	38,223.3	8.854	40,402.7
5200	8.833	41,844.4	9.464	43,974.3	13.223	55,957.4	14.945	66,984.0	8.734	39,965.1	8.873	42,175.5
5400	8.852	.....	9.512	.....	13.305	.....	14.982	.....	8.787	.....	8.891	
5600	8.869	.....	9.557									
5800	8.886	.....	9.602									
6000	8.903	.....	9.695									
6200	8.918	.....	9.686									
6400	8.933	....	9.727									

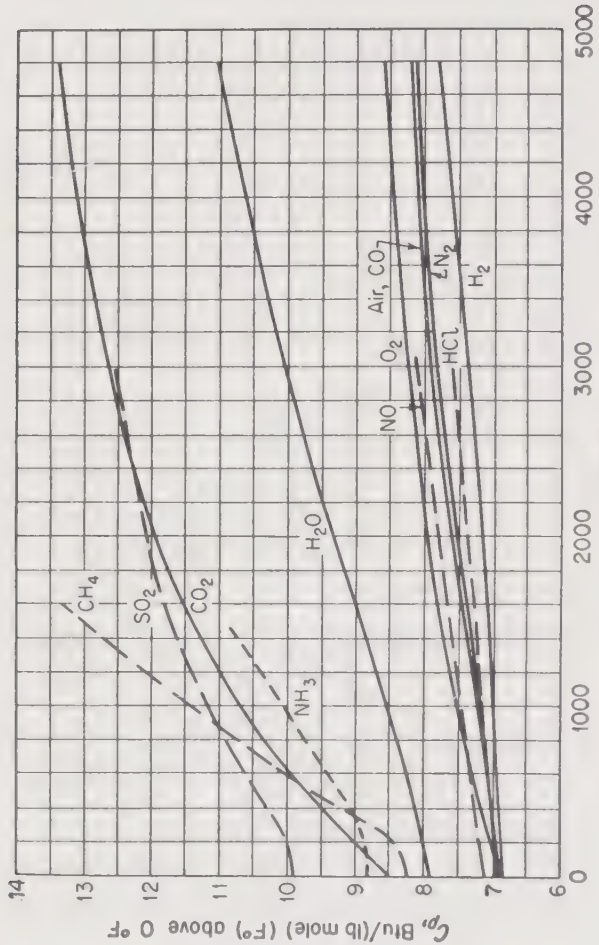
* Point values of heat capacities of nitrogen, oxygen, water vapor, carbon dioxide, hydrogen, and carbon monoxide were abridged from Keenan and Kaye, "Gas Tables," John Wiley & Sons, Inc., New York, 1948. Copyright, 1948, by Joseph H. Keenan and Joseph Kaye.

Mean values for nitrogen, oxygen, water vapor, carbon dioxide, hydrogen, carbon monoxide, and air were calculated from data in the Keenan and Kaye "Gas Tables." Values for the other gases were compiled from several sources which showed serious disagreement in some cases. The values for these gases must therefore be considered less reliable.

MEAN MOLAL HEAT CAPACITIES OF GASES ABOVE 0°F

t = °F $\bar{C}_p$ = Btu/(lbmole)(F°)

t	N_2	O_2	H_2O	CO_2	H_2	CO	CH_4	SO_2	NH_3	HCl	NO	Air
0	6.94	6.92	7.93	8.50	6.86	6.92	8.25	9.9	8.80	6.92	7.1	6.94
200	6.96	7.03	8.04	9.00	6.89	6.96	8.42	10.0	8.85	6.96	7.2	6.97
400	6.98	7.14	8.13	9.52	6.93	7.00	9.33	10.3	9.05	7.01	7.2	7.01
600	7.02	7.26	8.25	9.97	6.95	7.05	10.00	10.6	9.40	7.05	7.3	7.07
800	7.08	7.39	8.39	10.37	6.97	7.13	10.72	10.9	9.75	7.10	7.3	7.15
1000	7.15	7.51	8.54	10.72	6.98	7.21	11.45	11.2	10.06	7.15	7.4	7.23
1200	7.23	7.62	8.69	11.02	7.01	7.30	12.13	11.4	10.43	7.19	7.5	7.31
1400	7.31	7.71	8.85	11.29	7.03	7.38	12.78	11.7	10.77	7.24	7.6	7.39
1600	7.39	7.80	9.01	11.53	7.07	7.47	13.38	11.8	.....	7.29	7.7	7.48
1800	7.46	7.88	9.17	11.75	7.10	7.55	.....	12.0	.....	7.33	7.7	7.55
2000	7.53	7.96	9.33	11.94	7.15	7.62	.....	12.1	.....	7.38	7.8	7.62
2200	7.60	8.02	9.48	12.12	7.20	7.68	.....	12.2	.....	7.43	7.8	7.69
2400	7.66	8.08	9.64	12.28	7.24	7.75	.....	12.3	.....	7.47	7.9	7.75
2600	7.72	8.14	9.79	12.42	7.28	7.80	.....	12.4	.....	7.52	8.0	7.81
2800	7.78	8.19	9.93	12.55	7.33	7.86	.....	12.5	.....	7.57	8.0	7.86
3000	7.83	8.24	10.07	12.67	7.38	7.91	.....	12.5	.....	7.61	8.1	7.92
3200	7.87	8.29	10.20	12.79	7.43	7.95	.....	....	.....	....	...	7.96
3400	7.92	8.34	10.32	12.89	7.48	8.00	.....	....	.....	....	...	8.01
3600	7.96	8.38	10.44	12.98	7.53	8.04	.....	....	.....	....	...	8.05
3800	8.00	8.42	10.56	13.08	7.57	8.08	.....	....	.....	....	...	8.09
4000	8.04	8.46	10.67	13.16	7.62	8.11	.....	....	.....	....	...	8.13
4200	8.07	8.50	10.78	13.23	7.66	8.14	.....	....	.....	....	...	8.16
4400	8.10	8.54	10.88	13.31	7.70	8.18	.....	....	.....	....	...	8.19
4600	8.13	8.58	10.97	13.38	7.75	8.20	.....	....	.....	....	...	8.22
4800	8.16	8.62	11.08	13.44	7.79	8.23	.....	....	.....	....	...	8.26



Mean molal heat capacities of gases above 0°F.

Appendix Q

SOLUBILITIES OF INORGANIC COMPOUNDS IN WATER*

Solubility in g/100 g water (based on anhydrous compound)

Compound	0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C	100°C
NH_4Br	60.6	68	75.5	83.2	91.1	99.2	107.8	116.8	126	135.6	145.6
NH_4Cl	29.4	33.3	37.2	41.4	45.8	50.4	55.2	60.2	65.6	71.3	77.3
NH_4NO_3	118.3	.....	192	241.8	297.0	344.0	421.0	499.0	580.0	740.0	871.0
$Ca(OH)_2$	0.185	0.176	0.165	0.153	0.141	0.128	0.116	0.106	0.094	0.085	0.077
$CaSO_4$	0.1759	0.1928	.....	0.2090	0.2097	.....	0.2047	0.1966	.....	.....	0.1619
$FeCl_3$	74.4	81.9	91.8	.....	.....	315.1	.....	.....	525.8	.....	535.7
$FeCl_2$	.....	64.5	.....	73.0	77.3	82.5	88.7	.....	100	105.3	105.8
$FeSO_4$	15.65	20.51	26.5	32.9	40.2	48.6	.....	50.9	43.6	37.3	
$MgBr_2$	91.0	94.5	96.5	99.2	101.6	104.1	107.5	.....	113.7	.....	120.2

APPENDIX Q (*Continued*)

Compound	0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C	100°C
$MgCl_2$	52.8	53.5	54.5	.....	57.5	.....	61.0	.....	66.0	.....	73.0
$Mg(OH)_2$	.....	.....	0.0009[18°]								
$Mg(NO_3)_2$	66.55	.....	.....	.....	84.74	.....	.....	.....	.....	137	
$MgSO_4$	40.8	42.2	44.5	45.3	45.6	50.4	53.5	59.5	62.9	69.0	68.3
K_2CO_3	105.5	108	110.5	113.7	116.9	121.2	126.8	133.1	139.8	147.5	155.7
$KHCO_3$	22.4	27.7	33.2	39.1	45.4	.....	60.0				
KCl	27.6	31.0	34.0	37.0	40.0	42.6	45.5	48.3	51.1	54.0	56.7
KNO_3	13.3	20.9	31.6	45.8	63.9	85.5	110.0	138	169	202	246
K_2SO_4	7.35	9.22	11.11	12.97	14.76	16.50	18.17	19.75	21.4	22.8	24.1
$NaHCO_3$	6.9	8.15	9.6	11.1	12.7	14.45	16.4				
Na_2CO_3	7	12.5	21.5	50.5	48.5	.....	46.4	.....	45.8	.....	45.5
NaCl	35.7	35.8	36.0	36.3	36.6	37.0	37.3	37.8	38.4	39.0	39.8
NaOH	42	51.5	109	119	129	145	174	.....	.....	313	347
$NaNO_3$	73	80	88	96	104	114	124	.....	148	.....	180
Na_3PO_4	1.5	4.1	11	20	31	43	55	.....	81	.....	108
Na_2S	.....	15.42	18.8	22.5	28.5	36.4	39.1	43.31	49.14	57.28	
Na_2SO_3	13.9	20	26.9	36	28	28.2	28.8	.....	28.3		
Na_2SO_4	19.5	30	44	40.8	48.8	46.7	45.3	.....	43.7	.....	42.5
$Zn(NO_3)_2$	94.78	.....	118.3	.....	206.9						
$ZnSO_4$	41.9	47	54.4	.....	70.1	76.8	.....	.....	86.6	83.7	80.8

* From N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, by permission of the publishers.

Appendix R

SOLUBILITIES OF GASES IN WATER*

$p = Hx$ p = partial pressure of gas, atm
x = mole fraction of gas in liquid
H = Henry's-law constant
Note: Values tabulated are $10^{-3} \times H$

Gas	0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C	100°C
Air	43.2	54.9	66.4	77.1	87.0	94.6	101	105	107	108	107
CO_2	0.728	1.04	1.42	1.86	2.33	2.83	3.41				
CO	35.2	44.2	53.6	62.0	69.6	76.1	82.1	84.5	84.5	84.6	84.6
H_2	57.9	63.6	68.3	72.9	75.1	76.5	76.5	76.1	75.5	75.1	74.5
H_2S	0.268	0.367	0.483	0.609	0.745	0.884	1.03	1.19	1.35	1.44	1.48
NO	16.9	21.8	26.4	31.0	35.2	39.0	41.8	43.8	44.8	45.2	45.4
N_2	52.9	66.8	80.4	92.4	104	113	120	125	126	126	126
N_2O	.....	1.41	1.98	2.59							
O_2	25.5	32.7	40.1	47.5	53.5	58.8	62.9	66.3	68.7	69.9	70.1

* From John H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950. Data are from the sources listed below: air: 1; CO_2: 4, 15; CO: 6; H_2: 5, 8, 9; HCl: 6; H_2S: 7; NH_3: 2, 3; NO: 1, 5; N_2: 5, 6, 9, 10; N_2O: 11, 12; O_2: 5, 6, 9, 10, 13, 14; SO_2: 2.

1. Winkler, *Ber.*, vol. 34, p. 1408, 1901.
2. Sherwood, *Ind. Eng. Chem.*, vol. 17, p. 745, 1925.
3. Breitenbach, *Univ. Wisconsin Eng. Expt. Sta. Bull. Ser.* 68.
4. Bohr, *Ann. Physik*, vol. 68, p. 500, 1899.
5. Winkler, *Z. physik. Chem.*, vol. 9, p. 171, 1892.
6. Cassuto, *Physik. Z.*, vol. 5, p. 233, 1904.
7. Winkler, *Matemat. Természettud. Értesitö Magyar Tudományos Akad. III Osztályának Folyóirata*, vol. 25, p. 86, 1907.
8. Winkler, *Ber.*, vol. 24, p. 89, 1891.
9. Winkler, *Math. naturw. Ber. Ungarn.*, vol. 9, p. 195, 1892.
10. Winkler, *Ber.*, vol. 24, p. 3602, 1891.
11. Geffcken, *Z. physik. Chem.*, vol. 49, p. 257, 1904.
12. Kunerth, *Phys. Rev.*, vol. 19, p. 512, 1922.
13. Winkler, *Z. physik. Chem.*, vol. 55, p. 344, 1906.
14. Winkler, *Ber.*, vol. 22, p. 1764, 1889.
15. Wiebe and Gaddy, *J. Am. Chem. Soc.*, vol. 61, p. 315, 1939; vol. 62, p. 815, 1940.

APPENDIX B (*Continued*)

SOLUBILITY OF SO_2 IN WATER

Partial pressure of SO_2, mm Hg

Wt SO_2/100 wt H_2O	0°C	7°C	10°C	15°C	20°C	30°C	40°C	50°C
20	646	657						
15	474	637	726					
10	308	417	474	567	698			
7.5	228	307	349	419	517	688		
5.0	148	198	226	270	336	452	665	
2.5	69	92	105	127	161	216	322	458
1.5	38	51	59	71	92	125	186	266
1.0	23.3	31	37	44	59	79	121	172
0.7	15.2	20.6	23.6	28.0	39.0	52	87	116
0.5	9.9	13.5	15.6	19.3	26.0	36	57	82.0
0.3	5.1	6.9	7.9	10.0	14.1	19.7		
0.2	2.8	3.7	4.6	5.7	8.5	11.8	.....	31.0
0.15	1.9	2.6	3.1	3.8	5.8	8.1	12.9	20.0
0.10	1.2	1.5	1.75	2.2	3.2	4.7	7.5	12.0
0.05	0.6	0.7	0.75	0.8	1.2	1.7	2.8	4.7
0.02	0.25	0.3	0.3	0.3	0.5	0.6	0.8	1.3

SOLUBILITY OF HCl IN WATER

Partial pressure of HCl, mm Hg

Wt HCl/100 wt H_2O	0°C	10°C	20°C	30°C	50°C	80°C	110°C
78.6	510	840					
66.7	130	233	399	627			
56.3	29.0	56.4	105.5	188	535		
47.0	5.7	11.8	23.6	44.5	141	623	
38.9	1.0	2.27	4.90	9.90	35.7	188	760
31.6	0.175	0.43	1.00	2.17	8.9	54.5	253
25.0	0.0316	0.084	0.205	0.48	2.21	15.6	83
19.05	0.0056	0.016	0.0428	0.106	0.55	4.66	28
13.64	0.00099	0.00305	0.0088	0.0234	0.136	1.34	9.3
8.70	0.000118	0.000583	0.00178	0.00515	0.0344	0.39	3.10
4.17	0.000018	0.000069	0.00024	0.00077	0.0064	0.095	0.93
2.04	.....	0.0000117	0.000044	0.000151	0.00140	0.0245	0.280

APPENDIX R (*Continued*)

SOLUBILITY OF NH_3 IN WATER

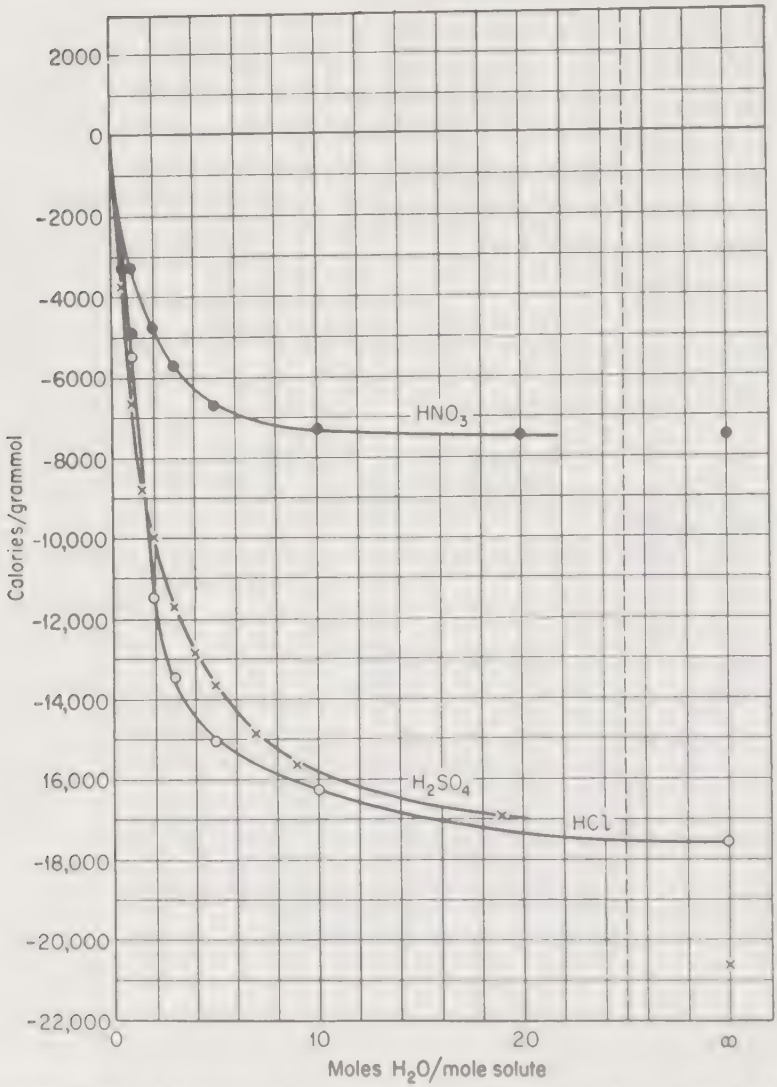
Partial pressure of NH_3, mm Hg

Wt NH_3/100 wt H_2O	0°C	10°C	20°C	25°C	30°C	40°C	50°C	60°C
100	947							
90	785							
80	636	987						
70	500	780						
60	380	600	945					
50	275	439	686					
40	190	301	470	....	719			
30	119	190	298	....	454	692		
25	89.5	144	227	....	352	534	825	
20	64	103.5	166	....	260	395	596	834
15	42.7	70.1	114	....	179	273	405	583
10	25.1	41.8	69.6	....	110	167	247	361
7.5	17.7	29.9	50.0	....	79.7	120	179	261
5	11.2	19.1	31.7	....	51.0	76.5	115	165
4	.....	16.1	24.9	....	40.1	60.8	91.1	129.2
3	.....	11.3	18.2	23.5	29.6	45	67.1	94.3
2.5	.....	.....	15.0	19.4	24.4	(37.6)*	(55.7)	77.0
2	.....	.....	12.0	15.3	19.3	(30.0)	(44.5)	61.0
1.6	.....	.....	.....	12.0	15.3	(24.1)	(35.5)	48.7
1.2	.....	.....	.....	9.1	11.5	(18.3)	(26.7)	36.3
1.0	.....	.....	.....	7.4	.....	(15.4)	(22.2)	30.2
0.5	.....	.....	.....	3.4				

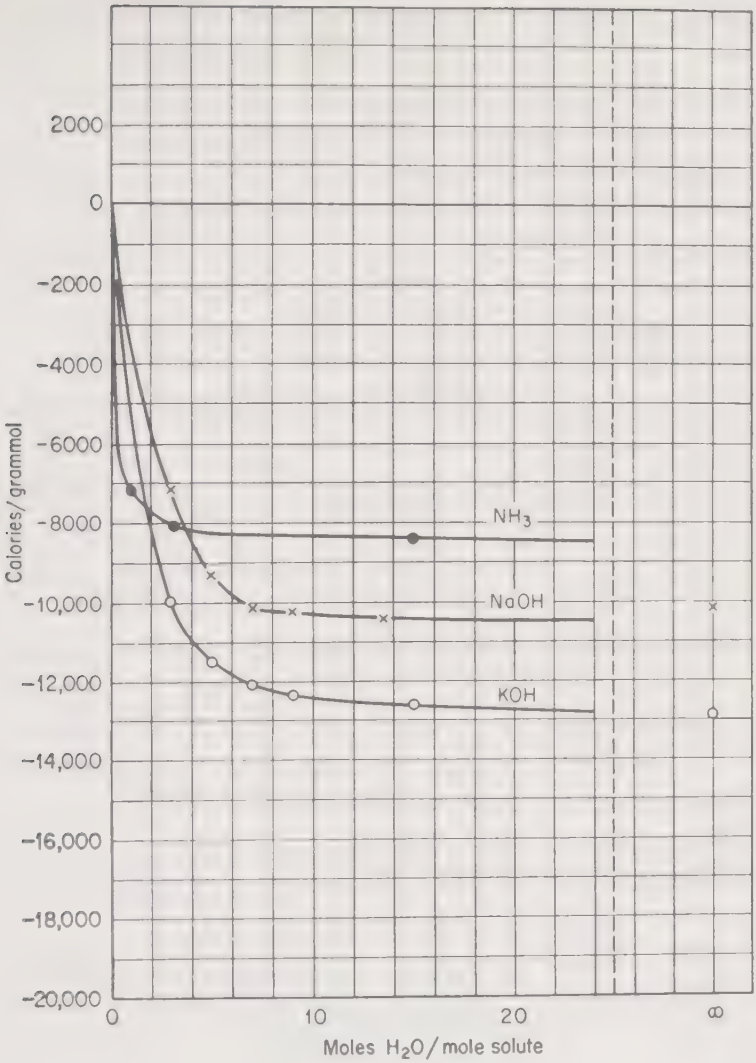
* Extrapolated values.

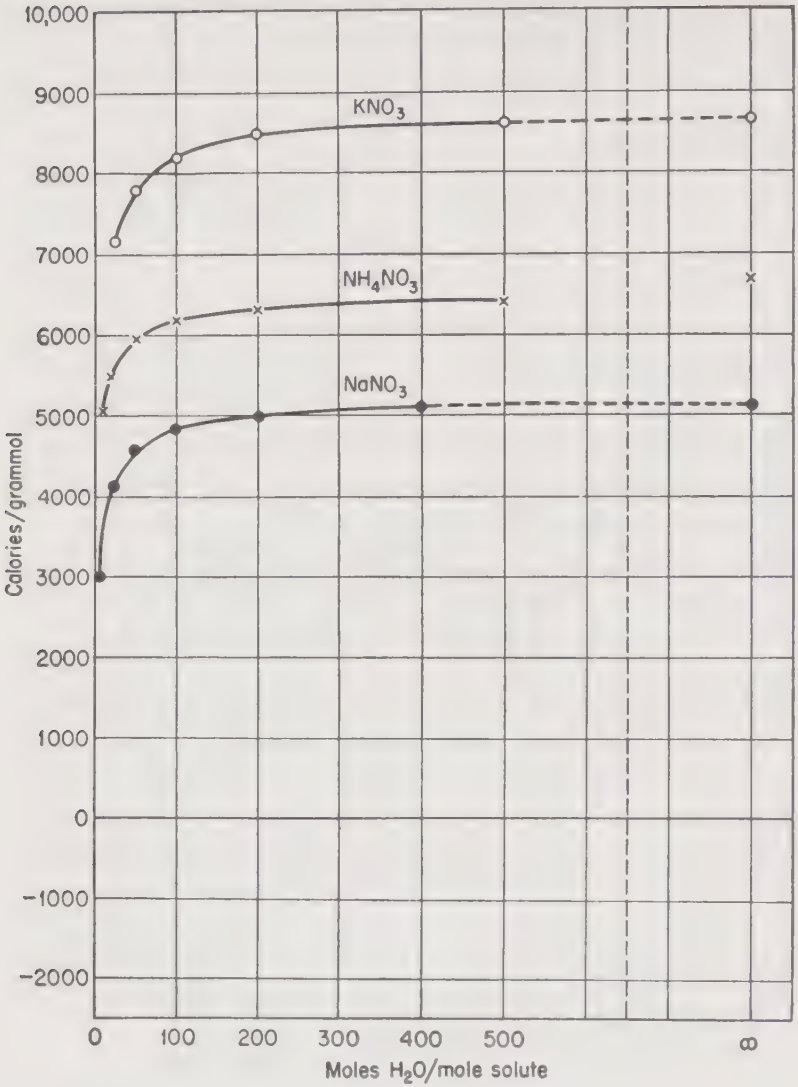
Appendix S

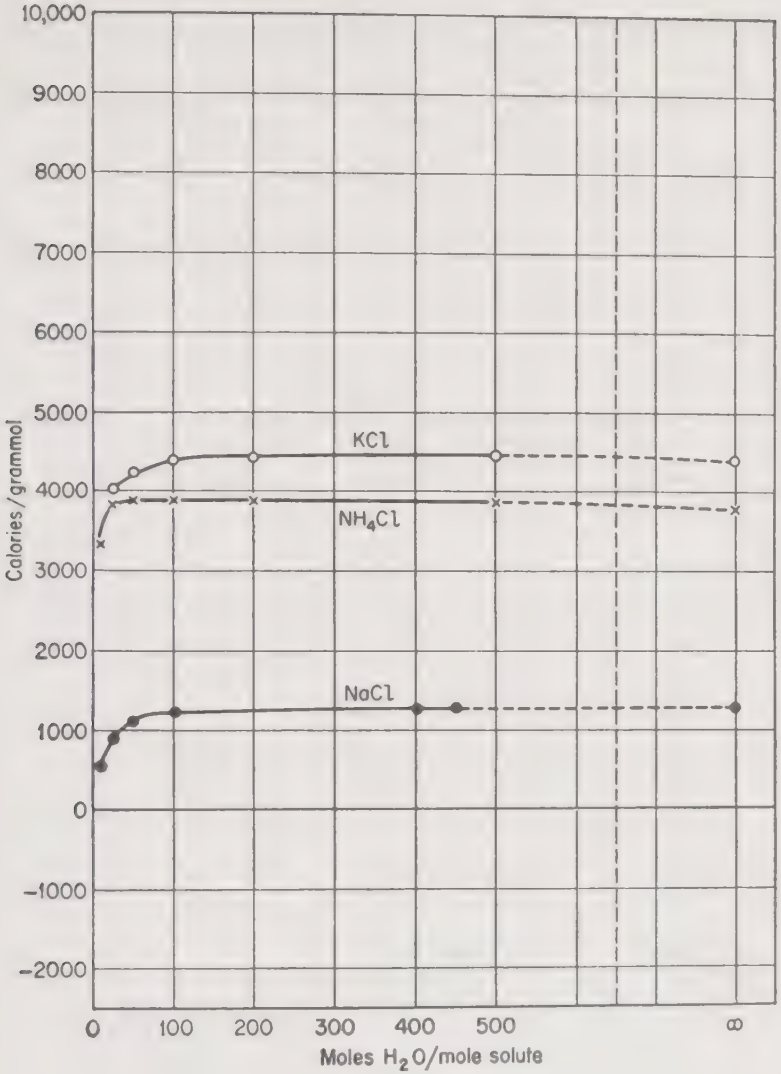
INTEGRAL HEATS OF SOLUTION*

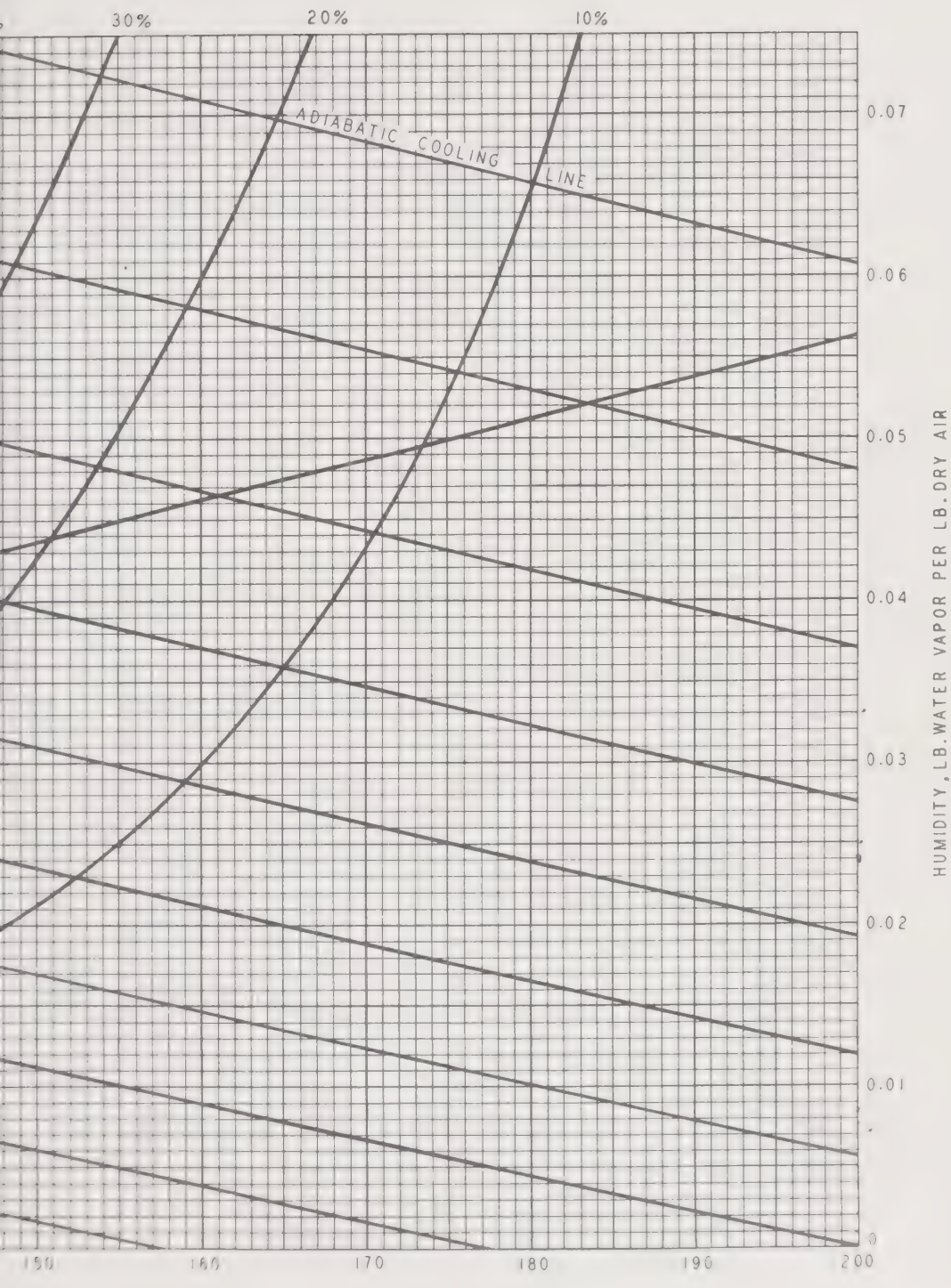


* Prepared from information in "International Critical Tables," vol. 5, McGraw-Hill Book Company, Inc., New York.


2000
0
-2000
-4000
-6000
-8000
-10,000
-12,000
-14,000
-16,000
-18,000
-20,000
Calories/grammol
NH3
NaOH
KOH
0
10
20
∞
Moles H2O/mole solute


10,000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
−2000
Calories/grammol
KNO3
NH4NO3
NaNO3
0
100
200
300
400
500
∞
Moles H2O/mole solute


10,000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
−2000
Calories / grammol
KCl
NH4Cl
NaCl
0
100
200
300
400
500
∞
Moles H2O/mole solute


30%
20%
10%
ADIABATIC COOLING LINE
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
150
160
170
180
190
200
HUMIDITY, LB. WATER VAPOR PER LB. DRY AIR

Appendix U

SELECTED PROBLEM ANSWERS

1-8. 0.813 Kg/(m²)(sec)
1-16. *a.* 20.26%w
b. 14.67 lb salt/ft³ soln
1-24. 6.98 ft³/lbmole
2-4. *Basis:* 100 lb
a. 3.13 lbatom
b. 1.56 lbatom
c. 2.01
d. CaC_2
2-12. *Basis:* 7 mole outlet gas
a. 1.875 mole O_2
b. 5.5 mole O_2
c. 9.375 mole O_2
d. 9.375 mole O_2
e. None
f. 0%
2-20. 0.986 atm
2-28. *a.* 43.5 ft³ O_2/min
b. 308 ft³ air/min
c. When adding volumes, all gases must be at same t and p.
2-37. *a.* 4.01 psia
b. 0.88 lb H_2O condensed
2-44. *a.* 470.3 ft³
b. 125 mm Hg
c. 36 lb H_2O
3-4. 7.01
3-12. 0.518 lb H_2O removed
3-19. 20% unburned
3-27. 39.9% excess air
4-5. *a.* C_p = 11.56 cal/(gmole)(C°)
b. C_p = 11.18 cal/(gmole)(C°)
c. Q = 2515 Btu
4-9. *a.* 74,429 cal released
b. 74,430 cal released
4-16. *a.* −35,002 cal/gmole of C_5H_{12}
b. −32,037 cal/gmole
4-28. 156,410 cal
5-8. *a.* 1.2088 mole
b. 0.1319
c. 24.54 lb CCl_4
30.43 lb air
54.97 total lb
d. 0.8064
e. 108.7°F
f. 501.7 ft³
g. 45%
h. 71°F
i. 75°F
j. 79°F
5-15. *a.* 176.7 lb
b. 0.0131 lb H_2O/lb dry air
5-25. 74.5% absorbed
6-3. *a.* 26.2 mole air supplied
b. 82.6% of maximum heat released
6-10. *a.* 2880 Btu in sensible heat
b. 1222 Btu in unburned CO
6-14. *a.* 69.4% ash, 30.6% C
b. 33,585 ft³
c. 1,218,000 Btu
d. 6.31%
e. 8.43%
f. 14.35%
6-29. 51.6%
6-34. *a.* 0.206 mole SO_3
b. The converter-gas (SO_3-free) analysis is the same as the exit-gas analysis.
c. 206.3 lb H_2SO_4 (100%) leaving
d. 74,000 Btu released

Appendix V

SELECTED PROBLEM SOLUTIONS

1-4. $\dfrac{0.7896\ \text{g/cm}^3}{1.0000\ \text{g/cm}^3} = 0.7896 \qquad 15°/4°$

$$(1.2061)\left(\frac{1.0000\ \text{g}}{\text{cm}^3}\right) = \frac{1.2061\ \text{g}}{\text{cm}^3}$$

$$\left(\frac{1.2061\ \text{g}}{\text{cm}^3}\right)\left(\frac{10^3\ \text{cm}^3}{\text{liter}}\right)\left(\frac{28.3\ \text{liters}}{\text{ft}^3}\right)\left(\frac{1\ \text{lb}}{454\ \text{g}}\right) = \frac{75.3\ \text{lb}}{\text{ft}^3}$$

1-12. *a.* $\dfrac{25}{75} = 0.333\ \dfrac{\text{lb salt}}{\text{lb } H_2O}$

$$\frac{75}{25} = 3.00\ \frac{\text{lb } H_2O}{\text{lb salt}}$$

$$\frac{(75)(100)}{100} = 75\%\text{w } H_2O$$

b. $(75)(1 - 0.4) = 45$ lb H_2O left

$$\frac{(25)(100)}{70} = 35.71\%\text{w salt}$$

c. Basis of calculation: 100 lb of solution

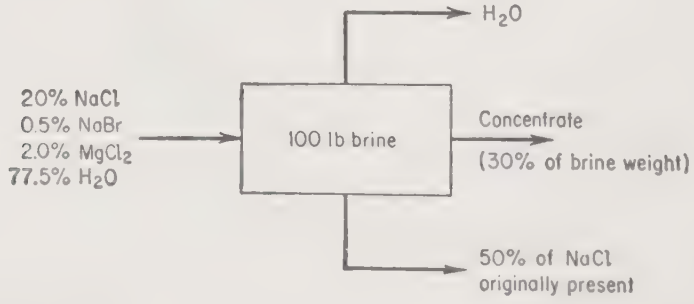
$75 - 40 = 35$ lb H_2O left

$$\frac{(25)(100)}{60} = 41.67\%\text{w salt}$$

d. $\dfrac{25}{(100 - W)(100)} = 60$

$W = 58.33$ lb of H_2O evap

1-20. *Basis:* 100 lb brine



a. 100 lb

b. 200 lb

c. 2 lb
d. 0.5 lb
e. 77.5 lb
f. (0.5)(20) = 10 lb NaCl ppt
100 − (0.3)(100) − 10 = 60 lb H_2O evap
(0.3)(100) = 30 lb concentrate

1-25. If we can find the unit cost of *A*, *B*, and *C*, we can check the most recent statement. Let *a*, *b*, and *c* equal the costs of *A*, *B*, and *C*, respectively, in \$/ton. Then,

$$0.3a + 0.18b + 0.69c = 589.80$$
$$0.2a + 0.24b + 0.40c = 461.60$$
$$0.21a + 0.30b + 0.66c = 654.60$$

Solving simultaneously,

$$a = \$220/\text{ton } A$$
$$b = \$840/\text{ton } B$$
$$c = \$540/\text{ton } C$$

Then,
(5 tons)[(0.06)(220) + (0.13)(840) + (0.19)(540)] = \$1125.00
Bill is correct.

2-8. $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

a. NaOH: 40
H_2SO_4: 98
Na_2SO_4: 142
H_2O: 18

b. Molecules H_2SO_4 = 1
Molecules NaOH = 2
Molecules H_2O = 2
Molecules Na_2SO_4 = 1

c. $\dfrac{12.12 \times 10^{23} \text{ molecules NaOH reacting}}{\text{mole } H_2SO_4 \text{ reacting}}$

$\dfrac{6.06 \times 10^{23} \text{ molecules } Na_2SO_4 \text{ formed}}{\text{mole } H_2SO_4 \text{ reacting}}$

$\dfrac{12.12 \times 10^{23} \text{ molecules } H_2O \text{ formed}}{\text{mole } H_2SO_4 \text{ reacting}}$

d. $\dfrac{2 \text{ gmole NaOH}}{\text{gmole } H_2SO_4}$

$\dfrac{1 \text{ gmole } Na_2SO_4}{\text{gmole } H_2SO_4}$

$\dfrac{2 \text{ gmole } H_2O}{\text{gmole } H_2SO_4}$

e. $\dfrac{2 \text{ lbmole NaOH}}{\text{lbmole } H_2SO_4}$

$\dfrac{1 \text{ lbmole } Na_2SO_4}{\text{lbmole } H_2SO_4}$

$\dfrac{2 \text{ lbmole } H_2O}{\text{lbmole } H_2SO_4}$

f. 1 kgmole H_2SO_4 = 98 kg
Then: 80 kg NaOH reacting
142 kg Na_2SO_4 formed
36 kg H_2O formed

2-16. *a.* $C = \frac{5}{9}(F - 32) = \frac{5}{9}(-32) = -17.7°C$

Temperature scale	Temperature	
F	0	100
C	−17.7	37.7
R	460	560
K	255.3	310.8

b. Change is 100 F° = 100 R° = 37.8 − (−17.7) = 55.5 C° = 55.5 K°

c. $(\frac{5}{9})(100\ F°) = 55.5\ C° = 55.5\ K°$

2-24. V = molar volume

a. $V = (22.4)(\frac{273}{273})(\frac{1}{1}) = 22.4$ liters $\quad N = \dfrac{100}{22.4} = 4.46$ mole

b. $V = (22.4)(\frac{460}{492})(\frac{1}{1}) = 20.9$ liters $\quad N = \dfrac{100}{20.9} = 4.78$ mole

c. $V = (22.4)(\frac{373}{273})(\frac{760}{10}) = 2325.9$ liters $\quad N = \frac{10}{2326} = 0.0430$ mole

d. $V = (22.4)\left(\dfrac{560}{492}\right)\left(\dfrac{14.7}{100}\right) = 3.75$ liters $\quad N = \dfrac{100}{3.75} = 26.7$ mole

e. No

2-32. *Basis:* 1 mole SO_2

a. $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

$\frac{1}{2}$ mole O_2 is needed to burn 1 mole SO_2.

With 100% excess, 1 mole O_2 must be supplied.

When the reaction goes 60% to completion, 0.6 mole SO_2 reacts, leaving $1 - 0.6 = 0.4$ mole SO_2 and forming 0.6 mole SO_3. This uses 0.3 mole O_2, leaving $1 - 0.3 = 0.7$ mole O_2. The results are best presented in tabular form. In the table, the weight of each component is calculated by wt = (mole wt)(no. of moles). For SO_2 in the reactants, for example, (64 lb/mole)(1 mole) = 64 lb SO_2.

a,b.

Component	Reactants					Products			
	Mole wt	Mole	y	lb	z	Mole	y	lb	z
SO_2	64	1	0.5	64	0.67	0.4	0.236	25.6	0.267
O_2	32	1	0.5	32	0.33	0.7	0.411	22.4	0.233
SO_3	80	0	...	..	....	0.6	0.353	48.0	0.500
		2	1.0	96	1.00	1.7	1.00	96.0	1.000

In the table, y = mole fraction, z = weight fraction. Note that Σy and Σz always equal unity. Note also that the total weight of reactants (96 lb) equals the total weight of products.

c. Average molecular weight $= \dfrac{\text{total lb}}{\text{total mole}}$

Reactants: $M_{av} = \frac{96}{2} = 48$

Products: $M_{av} = 96/1.7 = 56.5$

d. Using the equation $p_A = y_A P$, the partial pressures of the components in the products are

$p_{SO_2} = (0.236)(2) = 0.427$ atm

$p_{O_2} = (0.411)(2) = 0.822$ atm

$p_{SO_3} = (0.353)(2) = 0.706$ atm

e. Basis: 100 lb SO_2

$$\left(\frac{100 \text{ lb } SO_2}{64 \text{ lb } SO_2/\text{mole } SO_2}\right)\left(\frac{1.7 \text{ mole product}}{\text{mole } SO_2}\right) = 2.66 \text{ mole product}$$

$$(2.66 \text{ mole})\left(\frac{(359 \text{ ft}^3/\text{mole})(530°\text{R})(760 \text{ mm Hg})}{(\text{mole})(492°\text{R})(735 \text{ mm Hg})}\right) = 1064 \text{ ft}^3$$

2-39. p_{H_2O} in $= \dfrac{0.01}{1.01} = 0.0099$ atm

$y \approx Y = 0.0099 =$ mole fraction of H_2O in entering gas

p_{H_2O} out $= 0.01962$ atm $= \dfrac{0.02}{1.02}$

$y_1 \approx Y_1 = \dfrac{0.01962}{100} = 0.0002 =$ mole fraction of H_2O in exit gas

H_2O condensed $= 0.0099 - 0.0002 = 0.0097$ mole

$(0.0097)(18) = 0.175$ lb condensed

3-8. *Basis:* 1000 lb product

Let $x =$ lb waste acid

$y =$ lb conc H_2SO_4

$z =$ lb conc HNO_3

$x + y + z = 1000$

$0.57x + 0.93y = 600$

$0.23x + 0.90z = 270$

Solving,

$x = 418.3$ lb

$y = 388.7$ lb

$z = 193.0$ lb

3-16. Let $x =$ wt $Na_2CO_3 \cdot 10H_2O$

$y =$ wt $Na_2SO_4 \cdot 10H_2O$

$x + y = 100$

$(^{106}/_{286})x + (^{142}/_{322})y = 39.6 = 0.371x + 0.441y$

Solving,

$x = 64.3$ g

$y = 35.7$ g

$$\frac{64.3/286}{35.7/322} = \frac{\text{mole } Na_2CO_3}{\text{mole } Na_2SO_4} = 2.03$$

3-23. $N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad K_p = \dfrac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$

Basis: 1 mole N_2 + 3 mole H_2 at the start

a. NH_3 formed $= 0.148$ mole

$0.148/2 = 0.074$ mole N_2 used

$1 - 0.074 = 0.926$ mole left

b. $(^3/_2)(0.148) = 0.222$ mole H_2 used

$3 - 0.222 = 2.778$ mole left

c.

Final gas	Mole	y	$p = 10y$
N_2.....	0.926	0.240	2.40
H_2.....	2.778	0.721	7.21
NH_3.....	0.148	0.0384	0.384
	3.852	0.9994	9.994

d. $K_p = \dfrac{(0.384)^2}{(2.40)(7.21)^3} = 1.64 \times 10^{-4}\text{atm}^{-2}$

e. If 2 mole N_2 and 3 mole H_2 are present at the start, let x = mole NH_3 formed

$2 - \frac{1}{2}x = N_2$ left $\quad 3 - \frac{3}{2}x = H_2$ left

Total mole present at equilibrium

N_2: $2 - \frac{1}{2}x$
H_2: $3 - \frac{3}{2}x$
NH_3: x
$5 - x$

Since $p_i = y_i P$, then $p_{N_2} = \dfrac{(2 - \frac{1}{2}x)(10)}{5 - x}$ atm, etc.

and $1.64 \times 10^{-4} = \dfrac{[x/(5 - x)]^2(10)^2}{[(2 - \frac{1}{2}x)(10)/(5 - x)][(3 - \frac{3}{2}x)^3(10)^3/(5 - x)]}$

This reduces to

$$2.77 \times 10^{-2} = \frac{x^2(5 - x)^2}{(4 - x)(2 - x)^3}$$

which is best solved by trial and error in the form

$$x = 0.1\sqrt{\frac{(2.77)(4 - x)(2 - x)^3}{(5 - x)^2}}$$

Assuming values of x under the square root and calculating x,

Trial	*Calculation*
2	0
0	0.1885
0.1	0.1756
0.15	0.169
0.165	0.1675

Therefore, $x = 0.167$ mole NH_3 formed

f. The limiting reactant is H_2.
Of 3 mole in, $(\frac{3}{2})(0.167) = 0.25$ mole used
Therefore, $0.25/3 = 8.339\%$ conversion

3-31. *Basis:* Quantities as given

$$x_{O_2} = \frac{n_{O_2}\text{ dissolved}}{n_{H_2O} + n_{O_2} + n_{H_2}} \approx \frac{n_{O_2}}{n_{H_2O}}$$

(The approximations are valid if not much O_2 and N_2 dissolve and not much water evaporates.)

a. $x_{O_2} = (0.033 \times 10^{-6})(5)(760)(0.21) = 26.3 \times 10^{-6}$
n_{O_2} dissolved $= (26.3 \times 10^{-6})(10) = 2.63 \times 10^{-4}$

b. $x_{N_2} = (0.0165 \times 10^{-6})(5)(760)(0.79) = 49.5 \times 10^{-6}$
n_{N_2} dissolved $= 4.95 \times 10^{-4}$
(Note that the partial pressures are valid if not much dissolves and not much water evaporates.)

c. Vapor pressure $H_2O = p_{H_2O} = 17.67$ mm Hg
Total $P = (5)(760)$ total $P - p_{H_2O} = p_{\text{dry air}} = (5)(760) - 18 = 3782$ mm Hg
n_{H_2O} evap $= (17.67/3782)(1) = 46.7 \times 10^{-4}$ mole

d. Net change in number of moles $= (2.63 + 4.95) \times 10^{-4}$ dissolved and 46.7×10^{-4} evaporated. Gas increases by 39.1×10^{-4} mole.

$$\text{Relative volume change} = \frac{(39.1 \times 10^{-4})(10^2)}{1} = 0.391\%$$

Initial volume $= (1)(22{,}400)(\frac{1}{5})(\frac{293}{273}) = 4807$ cm³
$(4807)(39.1 \times 10^{-4}) = 18.7$ cm³ increase

4-8. *a.* Let ΔH_1 = change in enthalpy of liquid going from 40°C to 100°C
ΔH_2 = heat of vaporization at 40°C
ΔH_3 = change in enthalpy of vapor going from 100°C to 40°C
ΔH_4 = heat of vaporization at 100°C
$\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$

$$\Delta H_1 = \int_{100}^{40} C_p \, dT = -(60)(0.44)$$

In like manner, $\Delta H_3 = (60)(0.32)$

Therefore, $\Delta H_2 = (86.5 + 60)(0.44 - 0.32) = \dfrac{93.7 \text{ cal}}{\text{g}}$

or, heat of vaporization at 40°C $= (93.7)(92) = \dfrac{8620 \text{ cal}}{\text{gmole}}$

b. H_{vap} at 40°C $= \left(\dfrac{8620 \text{ cal}}{\text{gmole}}\right)\left(\dfrac{1.8 \text{ (Btu) (gmole)}}{\text{(lbmole) (cal)}}\right) = \dfrac{15{,}516 \text{ Btu}}{\text{lbmole}}$

c. If $H_{18°C_{liq}} = 0$, then $H_{150°C_{vap}} = \Delta H$ (heat liquid to 40°C) + ΔH (vaporization at 40°C) + ΔH (heat vapor to 150°C)

$$H_{150°C} = (40 - 18)(0.44) + 93.7 + (150 - 40)(0.32) = \frac{138.6 \text{ cal}}{\text{g}}$$

Also, 12,751 cal/gmole, or 22,952 Btu/lbmole, or 249 Btu/lb

4-12.

Reaction	ΔH
$CH_4 + 2O_2 = CO_2 + 2H_2O(l)$	−212,798 cal/gmole
$2H_2O(l) = 2H_2O(g)$	(2)(10,519)
$CH_4 + 2O_2 = CO_2 + 2H_2O(g)$	−191,760 cal/gmole

where 10,519 = ΔH_f of $H_2O(g)$ − ΔH_f of $H_2O(l)$ = −57,798 − (−68,317)

4-20. *Basis:* 1 mole of CH_4

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

x	$2x$	x	$2x$
burned	used	formed	formed

Q = heat released $= (t_2 - t_1)\Sigma n\bar{C}_p$
O_2 added = 2 mole, $N_2 = (2)(79/21) = 7.52$ mole
Outlet gases:

		$\bar{C}_p$ =
O_2:	$2 - 2x = 2(1 - x)$	7.40
N_2:	7.52	7.09
CH_4:	$1 - x$	10.88
CO_2:	x	10.48
H_2O:	$2x$	8.35

$\Delta H = -212{,}798 + (2)(10{,}519) = -191{,}760$ for $H_2O(g)$

$Q = 191{,}760x = (400 - 18)\Sigma n\bar{C}_p$

$\Sigma n\bar{C}_p = (7.40)(2)(1 - x) + (7.09)(7.52) + (10.88)(1 - x) + 10.48x + (8.35)(2)(x) = 79.00 + 1.5x$

Therefore: $191{,}187x = 30{,}178$

$x = 0.158$

15.8% burned

4-26. *Basis:* 100 lb solution in

$^{1}\%_{40} = 0.25$ mole NaOH

$^{9}\%_{18} = 5.0$ mole H_2O

$$\frac{5.0}{0.25} = \frac{20 \text{ mole } H_2O}{\text{mole NaOH}}$$

Basis: 100 lb solution out

$^{5}\%_{40} = 1.26$ mole NaOH

$^{5}\%_{18} = 2.78$ mole H_2O

$$\frac{2.78}{1.25} = \frac{2.22 \text{ mole } H_2O}{\text{mole NaOH}}$$

Properties and Data:

Solution	%w NaOH	Temp	$\frac{\text{mole } H_2O}{\text{mole NaOH}}$	ΔH, of soln, Btu/lbmole NaOH	$\bar{C}_p$(20°C)
In	10	90	20.0	−18,880	0.88
Out	50	230	2.22	−11,160	0.80

Basis: 100 lb in

$(0.10)(100) = 0.5C$

$C = 20$ lb conc soln

$F - C = E = 80$ lb evap

Since $Q = \Delta H$, a process will be followed where ΔH values may be easily obtained.

Step 1. Cool 100 lb 10% solution from 90 to 65°F (18°C).

$\Delta H_1 = (100)(0.88)(65 - 90) = -2200$ Btu

Step 2. Evaporate 80 lb H_2O.

100 lb 10% soln = 10 lb NaOH + 90 lb $H_2O(l)$

$\Delta H = -(-18{,}880)(0.25) = 4720$ Btu

10 lb NaOH + 10 lb $H_2O(l) = 20$ lb 50% soln

$\Delta H = (-11{,}600)(0.25) = -2900$ Btu

80 lb $H_2O(l) = 80$ lb $H_2O(g)$

$\Delta H = (^{8}\%_{18})(10{,}519)(1.8) = 84{,}152$ Btu

$\Delta H_2 = 4720 + (-2900) + 84{,}152 = 85{,}972$ Btu

Step 3. Heat 20 lb 50% solution from 65 to 230°F.

$\Delta H_3 = (20)(0.80)(230 - 65) = 2640$ Btu

Step 4. Heat 80 lb $H_2O(g)$ from 65 to 212°F

$\Delta H_4 = (^{8}\%_{18})(8.04)(212 - 65) = 5253$ Btu

$Q = -2200 + 85{,}972 + 2640 + 5253 = 91{,}665$ Btu for 100 lb

$$Q = \left(\frac{91{,}665 \text{ Btu}}{100 \text{ lb}}\right)\left(\frac{2000 \text{ lb}}{\text{ton}}\right) = \frac{1{,}833{,}300 \text{ Btu}}{\text{ton}}$$

5-5. The data taken during the night are correct. We may therefore correlate the amount of feed and concentrate.

Time	Amount fed to evaporator	Amount of concentrate	Ratio E/C
4–5	(10,000 − 9000) + 5000 = 6000	5000 − 2000 = 3000	2
5–6	0 + 5000 = 5000	7500 − 5000 = 2500	2
6–7	5500	2750	2
7–8	4000	2000	2

We now make similar day-shift calculations. Set up in tabular form.

Time	Lb in buffer	Δ	E = 5000 − Δ	Lb in	C	E/C
8	9,500			12,250		
		500	4500		2250	2
9	10,000			14,500		
		0	5000		2500	2
10	10,000			17,000		
		1000	4000		1700	2.35*
11	11,000			18,700		
		400	4600		2300	2
12	11,400			21,000		
		200	4800		2700	1.78*
1	11,600			23,700		
		−200	5200		2300	2.26*
2	11,400			26,000		
		−800	5800		3200	1.81*
3	10,600			29,200		
		−600	5600		2800	2
4	10,000			32,000		

* Several values are off. The operator was a goldbrick. Exact data forged cannot be determined since one forged value may throw off values on either side.

5-12. $RH = p_w/p_0$

$$H = \frac{(p_w)(M_w)}{(P - p_w)(M_A)}$$

For $RH = 50\%$

t, °F	70	100	130
p_0, mm Hg	18.78	49.07	114.91
p_w, mm Hg	9.39	24.54	57.46

$t = 70°F$

$$H = \frac{(9.39)(18)}{(760 - 9.39)(28.9)} = \frac{0.0078 \text{ lb } H_2O}{\text{lb dry air}}$$

$t = 100°F$

$$H = \frac{(24.54)(18)}{(760 - 24.54)(28.9)} = \frac{0.0208 \text{ lb } H_2O}{\text{lb dry air}}$$

$t = 130°F$

$$H = \frac{(57.46)(18)}{(760 - 57.46)(28.9)} = \frac{0.0509 \text{ lb } H_2O}{\text{lb dry air}}$$

From the humidity chart

t	70	100	130
H	0.0080	0.0215	0.0560

Comparing values, it can be seen that the values are in close agreement except in the steeply sloping region.

5-20. *a.* In this case, since the composition of the liquid and K values are known, the vapor composition is obtained by simple multiplication.

$y_{c_3} = (2.7)(0.10) = 0.27$
$y_{c_4} = (1.2)(0.484) = 0.58$
$y_{c_5} = (0.36)(0.416) = 0.15$
$\Sigma y = 1.0$

b. If x = liquid mole fraction
y = vapor mole fraction
L = mole of liquid/100 total mole
Subscripts $3 = C_3$, $4 = C_4$, $5 = C_5$
Then $(x_3L + y_3)(100 - L) = 15$
$(x_4L + y_4)(100 - L) = 50$ Component balances
$(x_5L + y_5)(100 - L) = 35$
Also $\Sigma x = 1$ and $\Sigma y = \Sigma Kx = 1$
From $(x_3L + K_3x_3)(100 - L) = 15$

$$x_3 = \frac{15}{100K_3 + L(1 - K_3)}$$

Etc. for x_4 and x_5. From $\Sigma x = 1$,

$$\frac{15}{100K_3 + (1 - K_3)L} + \frac{50}{100K_4 + (1 - K_4)L} + \frac{35}{100K_5 + (1 - K_5)L} = 1$$

Solve by trial and error for correct L value:

	$L = 0$	10	40	60	80	$y = Kx$ for $L = 80$
$x_3 = \frac{15}{270 - 1.7L}$	0.056	0.059	0.074	0.089	0.112	0.302
$x_4 = \frac{50}{120 - 0.2L}$	0.417	0.424	0.446	0.463	0.481	0.577
$x_5 = \frac{35}{36 - 0.64L}$	0.972	0 825	0.568	0.470	0.401	0.144
Σx	1.445	1.308	1.088	1.022	0.994	$\Sigma y = 1.023$

Note: $\Sigma x = 0.994$ for $L = 80$, but $\Sigma y = 1.023$. There may be a closer value of Σy. From a cross plot, try $L = 75$. By similar calculations,

	x	y
C_3.....	0.105	0.283
C_4.....	0.476	0.571
C_5.....	0.417	0.150
	0.998	1.004

These values are closer. Therefore, $L = 75$ is more nearly correct.
Material-balance checks:
C_3: (75)(0.105) + (25)(0.283) = 14.95
C_4: (75)(0.476) + (25)(0.571) = 50.0
C_5: (75)(0.417) + (25)(0.150) = 35.03
99.98

6-6. *Basis:* 1 mole CH_4 burned
H_2O formed = 2 mole = H_2O in flue gas
p_{H_2O} = (0.05)(2310) = 115.5 mm Hg
We now find the volume occupied by the water at 275°F and its partial pressure:

$$[(2)(359)]\left(\frac{735}{492}\right)\left(\frac{760}{115.5}\right) = 7060 \text{ ft}^3 \text{ wet flue gas}$$

We could check the data with a different calculation.
Basis: 100 mole DFG

Gas	Moles	C	O_2	N_2
CO_2.....	7.49	7.49	7.49	0
CO.....	1.89	1.89	0.95	0
O_2.....	4.80	0	4.80	0
N_2.....	85.82	0	0	85.82
		9.38	13.24	85.82

O_2 in = (85.82)($2\frac{1}{79}$) = 22.82
O_2 out = 13.24
O_2 for H_2O = 22.82 − 13.24 = 9.58 (Note only 9.38 mole C, and so slight error in data)
N = total mole = 100 + (2)(9.38) = 118.76

$$P = (115.5)\left(\frac{118.76}{18.76}\right) = 732 \text{ mm Hg}$$

$V = [(118.76)(359)](\frac{760}{732})(\frac{735}{492})$ = 66,000 ft³ for 9.38 mole CH_4
or V = 7060 ft³ per mole CH_4

6-12. *Basis:* 100 mole DFG

Component	Moles	Mole C	Mole O_2
CO_2.....	14.5	14.5	14.5
O_2.....	3.76	0	3.76
N_2.....	81.74	0	0 (by difference)
	100.00	14.5	18.26

$(81.74)(21/79) = 21.7$ mole O_2 in
$21.7 - 18.26 = 3.44$ mole O_2 disappear
$(2)(2)(3.44) = 13.76$ lb net H_2 in coal

$$(14.5 \text{ mole C})\left(\frac{12 \text{ lb C}}{\text{mole C}}\right)\left(\frac{100 \text{ lb coal}}{80 \text{ lb C}}\right) = 216 \text{ lb coal fired}$$

$$\left(\frac{13.76}{216}\right)(100) = 6.37\% \text{ net hydrogen}$$

6-24. *Basis:* 100 mole SO_3-free BG

Component	Moles	S
SO_2	9.32	9.32
O_2	6.93	
N_2	83.75	
	100.00	9.32

O_2 in $= (83.75)(21/79) = 22.25$ mole
O_2 accounted for $= (9.32)(1\frac{1}{8}) + 6.93 = 19.73$ mole
O_2 used for $SO_3 = 22.25 - 19.73 = 2.52$ mole
$SO_3 = (2.52)(8/15) = 1.34$ mole
Total S burned $= 9.32 + 1.34 = 10.66$ mole

$$\left(\frac{1.34}{10.66}\right)(100) = 12.6\% \text{ of S goes to } SO_3$$

6-37. *Basis:* 100 lb pyrites
$(90)(64/120) = 48$ lb S
Let X = lb pure S.

$$\frac{X}{48 + X} = 0.06 \qquad X = 3.065 \text{ lb}$$

Basis: 100 lb is cinder
6 lb S in cinder. Of this 2.4 lb are in SO_3 and 3.6 lb are in FeS_2.
$SO_3 = (2.5)(80/32) = 6.0$ lb
$FeS_2 = (3.6)(120/64) = 6.76$ lb
The remaining cinder contains Fe_2O_3 and gangue. The total Fe:gangue ratio must be the same as in the pyrites.

$$\frac{\text{Fe}}{\text{G}} = \frac{90 - 48}{10} = 4.2 \text{ in pyrites}$$

Let Y = lb Fe_2O_3 in cinder
In cinder, Fe $= (6.76 - 3.6) + 112/160\,Y$
G $= 100 - (6.0 + 6.76 + Y)$

$$\text{Then } \frac{3.16 + 0.70Y}{87.24 - Y} = 4.2$$

and $Y = 74.1$ lb Fe_2O_3 G $= 87.24 - 74.1 = 13.14$ lb
Basis: 100 lb charge

$$\left(\frac{100}{103.065}\right)(3.065) = 2.97 \text{ lb S}$$

and $100 - 2.97 = 97.03$ lb pyrites, containing 9.70 lb G and 87.33 lb FeS_2

a. Cinder $= \left(\frac{9.70}{13.14}\right)(100) = 73.8$ lb by G balance

Checking Fe balance,

$$\text{Cinder} = \frac{(87.33)(^{56}/_{120})}{3.16 + (0.7)(74.1)}(100) = 74.2 \text{ lb}$$

(In following calculations, we use 74.0 lb)

$$\text{S fed} = (51.065)\left(\frac{100}{103.065}\right) = 49.6 \text{ lb}$$

S lost in cinder = (0.06)(74.0) = 4.44 lb

S into gas = 45.2 lb ≈ 1.412 lbmole

$$O_2 \text{ used for } Fe_2O_3 = \left(\frac{74.1}{160}\right)\left(\frac{3}{2}\right)(0.74) = 0.515 \text{ mole}$$

$$O_2 \text{ used for } SO_3 \text{ in cinder} = \left(\frac{6.0}{80}\right)\left(\frac{3}{2}\right)(0.74) = 0.083 \text{ mole}$$

Total O_2 in cinder = 0.598 mole

Basis: 100 mole SO_3-free BG

O_2 in = $(86.8)(^{21}/_{79})$ = 23.07 mole

O_2 out = 4.25 + 8.95 = 13.20 mole

O_2 for SO_3 in gas + O_2 in cinder = 23.07 − 13.20 = 9.87 mole

S in SO_2 = 4.25 mole

Basis: 100 lb charge

Let Z = mole SO_3-free BG

W = mole SO_3 in BG

Balance on S in BG:

$$1.412 = 0.0425Z + W$$

Balance on O_2 disappearance and O_2 in cinder:

$$0.0987Z = 0.598 + 1.5W$$

Solving simultaneously,

Z = 16.72 mole SO_3-free BG and W = 0.70 mole SO_3 in BG

$$\text{S fired} = \frac{49.6}{32} = 1.55 \text{ mole}$$

b. Per cent of S fired as SO_3 in BG is

$$\left(\frac{0.70}{1.55}\right)(100) = 45.1\%$$

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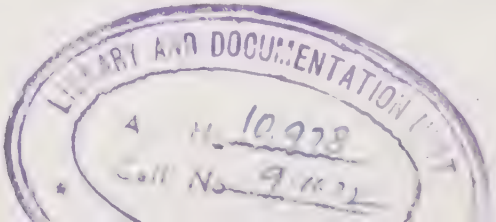
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